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Photochemical simulations of Titan's stratosphere

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PHOTOCHEMICAL SIMULATIONS OF TITAN'S STRATOSPHERE

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Samuel Michael Clegg

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Abstract

PHOTOCHEMICAL SIMULATIONS OF TITAN'S STRATOSPHERE

by Samuel M. Clegg

Laboratory photochemical simulations of the photolysis of acetylene were performed to characterize the production of the organic haze layers and hydrocarbons observed in the stratosphere of Titan, a satellite of Saturn. The size distribution of polyacetylene aerosols as a function of acetylene pressure was determined by scanning electron microscopy. As the acetylene pressure increased from 0.2 to 10 torr, the mean particle radius increased from 0.2 to 0.4 um. The overall all rate of aerosol appearance increased as the total pressure increased from 0 to 60 torr. The photolysis of acetylene also produced other hydrocarbons including ethane. The amount of ethane produced from the catalytic decomposition of methane by the photolysis of acetylene was studied. The results indicate that the catalytic decomposition of methane does not produce an increased amount of ethane, compared to the photolysis of acetylene alone.

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DEDICATION:

I would like to dedicate this thesis to my loving wife, Ann Marie Clegg, who has always been there to support and encourage.

I love you Ann.

"Therefore, since we have been justified through faith, we have peace with God through our Lord Jesus Christ, through whom we have gained access by faith into this grace in which we now stand. And we rejoice in the hope of the glory of God. Not only so, but we also rejoice in our sufferings, because we know that suffering produces perseverance; perseverance character; and character, hope. And hope does not disappoint us, because God has poured out his love into our hearts by the Holy Spirit, whom he has given us."

Romans 5:1-5 (NIV)

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1. Introduction

1.1. Characterization of Titan's Atmosphere

Titan is the largest of 17 satellites of the planet Saturn and it is the only satellite in the solar system that contains a substantial atmosphere. The Saturnian system was first discovered by the astronomer Galileo in 1610 and Titan was first identified as Saturn's largest satellite by Huygens in the 17th century.[1] The first recorded observation of Titan's atmosphere was made by Sola' in 1908, who observed that "Titan exhibited strong limb darkening."[2] He also claimed that Jupiter's Galilean satellites also had atmospheres because they portrayed the same limb darkening. However, these observations led Sola' to an incorrect conclusion regarding the Galilean satellites, which led to uncertainty in his claims about Titan. In 1944 Sola's claim that Titan had an atmosphere was verified by Kuiper, who identified methane peaks in the absorption spectrum of Titan and concluded that Titan's atmosphere was primarily methane.

The chemical evolution and exobiology of the atmosphere is of particular interest. The abundance of hydrocarbons and nitrogen in Titan's atmosphere along with photochemical activity could lead to the production of chemical compounds that are precursors to the evolution of life. However, the conditions on the surface are not likely to support life and life is not expected to have evolved on Titan. The study of the processes observed on Titan may lead to a better understanding of the origin of life on Earth since there are some similarities between the atmospheres. Titan's atmosphere is primarily composed of nitrogen, N_2, as is the Earth's atmosphere. It also contains a relatively large amount of methane that has been photolyzed by the solar flux over geologic time to produce larger hydrocarbons and polymers. The production of the polymers is believed to be responsible for the existence of an opaque, stratospheric haze layer that envelops the satellite, analogous to the Earth's ozone layer in that it absorbs much of the solar ultraviolet radiation.[3]

Some of the best scientific data currently available on Titan's atmosphere was gathered in 1980 by Voyagers 1 & 2. Before 1980, scientists were confined to ground-based and eventually orbital telescopic images that were restricted by interferences due the Earth's atmosphere and the distance from the Earth. In 1977, Voyagers 1 and 2 were launched from Kennedy Space Center to encounter Jupiter and the Saturnian system. The instruments on these probes allowed for better determination of many characteristics of Titan's atmosphere including it's composition and the temperature - pressure - altitude profile.

Voyagers 1 and 2 were identical probes that encountered the Saturnian system 9 months apart. The use of 2 identical probes and the time delay served many purposes including insurance against breakdowns in either probe and observing changes over the 9 month period. The mission priorities were not exactly the same and Voyager 2 did not spend as much time observing Titan.[4] Four of the instruments on Voyager were the Radio Science (RSS), Infrared Interferometer Spectrophotometer (IRIS), Ultraviolet Spectrophotometer (UVS), and Imaging Science (ISS).[3]

In the Radio Science experiments, Voyager emitted a radio signal that was monitored on Earth as the probe was occulted by Titan. The signal intensity would decrease as the density of the atmosphere through which the signal must travel increased and disappeared when the probe flew behind Titan's solid body. With this data, it was determined that Titan is the second largest satellite in the solar system with a radius of 2,575 km.[1]

The IRIS observations monitored the infrared emissions of the satellite and determined the thermal structure of Titan. The surface temperature was determined to be 94 K.[5] The atmosphere reaches a temperature minimum of approximately 70 - 75 K in the tropopause, at about 42 km altitude, and reaches a maximum of 170 K at about 200 km altitude.[5] The atmospheric pressure at the surface of Titan was determined to be 1.5 bar, 50% greater then the Earth's atmospheric pressure, and is about 1 mb at an altitude of 200 Km.[5] Titan's physical characteristics are summarized in Table 1.1.[6]

The sun was used as the light source for the UVS that monitored the ultraviolet spectrum of Titan to determine some of the components of the atmosphere. From the UVS data, modelers predicted that methane accounts for about 6% of the atmosphere.[2] Smaller amounts of larger hydrocarbons were also observed including ethylene and acetylene.[1]

The Imaging Science observations were completed by 2 different video cameras; a narrow angle camera and a wide angle camera with 0.4° and 3.2° fields of view, respectively.[7] These images allowed for the determination of Titan's shape and color. This instrument also allowed for determination of the size of the stratospheric aerosol particles by observing the light intensity at a specific wavelength as a function of the solar phase angle, the angle between the Sun, Titan, and Voyager.[8]

Combinations of the data also gave useful information. The RSS and the IRIS data were used to determine that the mean molecular weight of Titan's atmosphere is 28.6 atomic mass units (AMU).[3,6] With this result, modelers predicted that Titan's atmosphere contains between 76-99% nitrogen.[6] However, this is still only a prediction because nitrogen is spectroscopically transparent and could not be detected with the instrumentation on board Voyager. Modelers predicted that between 0-21% argon could be present in the Titan atmosphere as well. The argon atmospheric concentration is uncertain because it is also spectroscopically transparent and its molecular weight is close to that of nitrogen, N_2. Small amounts of carbon monoxide and carbon dioxide have also been detected. The source of these species is somewhat uncertain; it may be indigenous and outgassed from the frozen surface or it may have formed by the reaction of the atmospheric hydrocarbons and water. It has been suggested that icy impactors, such as comets, contribute the water and energy to facilitate the formation of carbon monoxide and carbon dioxide.[5] The equatorial abundance of a variety of observed compounds in the different atmospheric regions is compiled in Table 1.2.[6]

Methane in the stratosphere has been photolyzed over geologic time to produce larger hydrocarbons, primarily acetylene. Acetylene can further photolyze to produce other hydrocarbons and polymers, such as polyacetylene. It is believed that these polymers aggregate in the stratosphere to form the aerosol particles that are thought to make up the three stratospheric haze layers that envelop the satellite. The following is a discussion of the suggested photochemical process.

Methane can be photolyzed by the solar flux at wavelengths less then 145 nm.[9] When methane absorbs a photon, it will photodissociate to produce one of 4 possible intermediates.

$$CH_4 + h\nu \text{ --> } CH_3 + H \qquad (1)^{11}$$

$$\text{--> } CH_2 + H_2 \qquad (2)^{10}$$

$$\text{--> } CH_2 + 2H \qquad (3)^{10}$$

$$\text{--> } CH + H + H_2 \qquad (4)^{10}$$

These intermediates can react with other molecules or radicals to produce primarily acetylene and ethylene.[5]

$$2CH_4 \text{ --> } C_2H_2 + 3H_2 \qquad (5)^{10}$$

$$2CH_4 \text{ --> } C_2H_2 + 4H + H_2 \qquad (6)^{10}$$

$$2CH_4 \text{ --> } C_2H_4 + 2H + H_2 \qquad (7)^{10}$$

$$2CH_4 \text{ --> } C_2H_4 + 4H \qquad (8)^{10}$$

Acetylene can be photolyzed at wavelengths less than 210 nm to produce the following intermediates.

$$C_2H_2 + h\nu \text{ --> } C_2H + H \qquad (9)^{10}$$

$$\text{--> } C_2 + H_2 \qquad (10)^{10}$$

The quantum yields for reactions (9) and (10) are 0.06 and

0.10, respectively.[5] The primary product of the photolysis of acetylene is diacetylene (C_4H_2). Many other hydrocarbons are also produced by the photolysis of acetylene, including methane, ethane, ethylene, propane, and butane. When acetylene is photolyzed in the presence of diacetylene, triacetylene (C_6H_2) is produced, via Reaction (12). This progression continues to produce larger polymers, as follows.

$$C_2H + C_2H_2 \text{ --> } C_4H_2 + H \qquad (11)^{10}$$

$$C_2H + C_4H_2 \text{ --> } C_6H_2 + H \qquad (12)^{10}$$

$$C_2H + C_6H_2 \text{ --> } C_8H_2 + H \qquad (13)^{10}$$

$$C_2H + C_nH_2 \text{ --> } C_{n+2}H_2 + H \qquad (14)$$

Each of the products of reaction (11)-(14) are also reactive and can be photolyzed to produce other hydrocarbons and polymers. A short list of important reactions is compiled in Table 1.3. It has been suggested that most of the polyacetylene molecules produced do not become much larger than 8 carbons long because they would condense at the ambient conditions involved and be removed from the photochemical process.[5] Eventually the polymers will aggregate and form the aerosols that are believed to make up the three stratospheric haze layers. A diagram of the major hydrocarbon photochemical reactions of interest on Titan is shown in Fig. 1.1.[5,6]

The abundance of nitrogen in the atmosphere leads to the production of cyanide compounds and could be present in the polymers. However, molecular nitrogen is relatively inert and can only be photolyzed by short wavelength photons or energetic particles. Hydrogen cyanide has been observed on Titan and could also be involved in the photochemistry.

The composition of the aerosol particles is still uncertain. Originally, they were simply described as aggregates of polyacetylene molecules.[9] A study of the optical properties of Titan's atmosphere with the International Ultraviolet Explorer (IUE) determined that they are more characteristic of aggregates of polyethylene.[12] Hydrogen cyanide is also known to photolyze and produce poly-HCN molecules that could exist in the aerosol particles.[9,13] It is more likely that the composition of the aerosols is a mixture of polymer chains originating from acetylene, ethylene, and HCN.[9,13]

Analysis of Voyager's high phase angle data determined that there are two detached haze layers above the main haze layer that extend through the lower northern hemisphere and the entire southern hemisphere.[8] The main haze layer begins at an altitude of approximately 175 Km and the two detached haze layers exist at 300-350 Km and 450-500 Km.[3,8] The size and density of each haze layer decreases with altitude.

The aerosols are effective absorbers and scatterers of light, and therefore it is very difficult to study surface conditions by optical means.[14] However, the atmosphere becomes increasingly transparent between 17 and 20 um, and opaque again at wavelengths lower than 20 um.[15,16] The increasing opacity has been explained by either the increasing absorption of nitrogen and methane in the lower atmosphere or the presence of methane clouds in the tropopause. A plot of the optical depth as a function of altitude from Voyager data of Titan's equatorial region can be viewed in Lunine *et al.* (1989).[3]

The mean particle radius of the aerosols in the stratospheric haze layers has been studied in detail. Voyager 1's high-phase angle experiment measured the scattering of sunlight as the probe was occulted by Titan.[1] For a phase angle of 160 to 129° and a wavelength of 420 nm, the mean aerosol particle radius was between 0.25 and 0.3 um.[10,11] Voyager 2 performed the same experiment and determined that the mean aerosol particle radius ranged from between 0.25 and 0.5 um.[10] Further analysis of the Voyager high-phase angle data by Rages and Pollack (1983) determined that the mean particle radius was approximately 0.27 um and between 0.45 um and 0.8 um and suggests the possibility of a bimodal size distribution of aerosol particles.[8] Additional ground based studies of the polarization of reflected light determined that the mean particle radius was approximately 0.1 um.[9,14] The IUE measured the mean particle radius of the high altitude haze layer to be as small as 0.02 um and between 0.1 um and 0.5 um.[12] A possible explanation for the discrepancy in sizes is the presence of non-spherical aerosol particles or a variation in the size of the aerosols with altitude. Laboratory simulations of the production of these aerosols have been performed by photolyzing mixtures of acetylene and nitrogen at 185 nm. The resulting polyacetylene aerosol particles were allowed to settle out onto a glass cover slip, and imaged with a scanning electron microscope. Analysis of the polyacetylene aerosol particles determined that the size distribution was gaussian and the mean particle radius was 0.3 um.[9]

It has been suggested that Titan's atmosphere, at the observed surface temperature, methane partial pressure and a methane relative humidity of between 60% and 80%, could contain methane clouds similar to water clouds on Earth.[17] Voyager's IRIS data indicates a broad absorption between 17 and 50 um that could be due to the presence of condensed methane.[17] There is also evidence that the concentration of methane in the upper atmosphere is enough to suggest the presence of clouds in the tropopause, the region of the atmosphere where the temperature is at a minimum.[17] In addition to temperature and pressure considerations, the clouds need a source of methane. Models developed before and after the Voyager encounter suggest that a methane ocean could exist on the surface, similar to the oceans of water on Earth. Under these conditions, the lower atmosphere could become saturated with methane that could lead to condensation at the temperature minimum. Settling aerosol particles from the stratospheric haze layers could act as condensation nuclei in the formation of these clouds.

A model by Toon *et al.* (1988) suggests a much different type of cloud system then that observed on Earth. Using results from Voyager's RSS and IRIS data, their model suggests that the Titanian clouds consist of fewer and larger cloud particles then on Earth.[17] In order for clouds to exist at increased altitudes, an increased methane mixing ratio would be necessary.[17] Therefore, most of the clouds in the model exist lower than 10 Km and would not extend over 30 Km.[17] RSS data also suggests that the clouds are not continuous, but patchy. According to the model, the clouds on Titan would be characterized as a "raindrop sized fog" on Earth.[17] The Toon *et al.* (1988) model also suggests that a methane ocean is not as necessary as previously believed.[17] They argue that enough methane has been supplied by outgassing and photolyzed over geologic time, that an ocean on Titan would primarily consist of ethane mixed with a substantial amount of methane. The methane in the ocean would reach equilibrium with the atmosphere and become a source for the clouds. The ethane/methane ocean should also contain a relatively large amount of aerosols from the stratospheric haze layers.

The stratospheric haze layers give the satellite an asymmetric reddish color. The northern hemisphere is a darker red with a region over the northern pole that is five times darker then any other region of the atmosphere.[8] The reason for this brightness asymmetry is unknown. One hypothesis is that it is due to seasonal differences between the hemispheres, an effect observed on the Earth.[1] On the Earth the winter hemisphere tends to be brighter than the summer hemisphere because of the increase in snow and cloud cover. Other explanations include changes in the haze layer or underlying cloud deck.[1]

In October 1996, NASA and the European Space Agency (ESA) will conduct a joint exploration of the Saturnian system.[18] NASA is supplying Cassini (a Mariner Mark II spacecraft) and ESA is supplying Huygens, an atmospheric probe that will detach from Cassini and land on Titan. Cassini will make several Titan flybys to make observations and directional changes as it tours Saturn and its other satellites.[18] The Huygens Probe will land on Titan and make direct atmospheric studies as it descends through the atmosphere and at the surface.[18] Some of the mission objectives regarding Titan are to make measurements of the composition of the atmosphere as a function of the altitude, the composition of the stratospheric aerosols, the meteorological processes, and the surface conditions.[18] Cassini is planned to reach the Saturnian system by June 2004 and the mission will be completed by 2008.[18]

1.2. Research Objectives

Methane is believed to be the starting material that leads to the production of the stratospheric aerosols. The first step in the formation of these aerosols is the production of acetylene. The photolysis of acetylene primarily produces diacetylene, that in turn will produce triacetylene and larger polyacetylene* molecules as discussed

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*Aerosols produced from the photolysis of acetylene are called polyacetylene aerosol particles. However, the actual composition of the aerosols is unknown. It is more likely that they are a mixture of polymer chains of acetylene, ethylene, and hydrogen cyanide.

in section 1.1. It is believed that the polyacetylene molecules aggregate to produce aerosols similar to those observed on Titan. Observations of the stratospheric aerosols on Titan determined that the radius of the aerosols were between 0.25 and 0.5 um with particles as small as 0.02 um in the outer haze layers. One explanation for the range in particles is the presence of non-spherical particles. The observations of the smaller particles also suggests an altitude, and thus a pressure, dependence on the aerosol size.

Laboratory simulations of the production of polyacetylene aerosol particles as a function of the acetylene pressure will be performed. The results of these experiments will determine the size distribution dependence on the acetylene pressure and will better characterize the formation process as a function of altitude. This could help explain the range of aerosol particles observed on Titan. The number of particles per aggregate will also be examined.

The total pressure dependence of the overall rate of aerosol appearance will also be studied. The results of these experiments should determine if the total pressure effects the production of the polyacetylene aerosol particles. These results should also help determine how the total pressure could have effected the size of the aerosols discussed earlier.

The photolysis of acetylene produces other hydrocarbons including methane, ethane, ethylene, and propane. The quantity of a gas in planetary atmospheres is typically reported as the ratio of the gas of interest to the primary atmospheric component and is called a mixing ratio. The mixing ratio of ethane and propane in Titan's stratosphere is greater than in the tropopause, the region of the atmosphere where the temperature is a minimum.[5] The surface cannot be the source of the increased mixing ratio due to tropopause restrictions. As the gas travels up to the temperature minimum, only the vapor pressure of that gas at that temperature will remain in the gas phase and the excess will condense and settle to the surface. Therefore, the increased ethane and propane mixing ratio must be photochemically produced.

It has been suggested that the increased mixing ratio of ethane and propane was produced from the catalytic decomposition of methane by the photolysis of acetylene.[5,19] Previous experimental results determined that the photolysis of acetylene in the presence of methane will cause photosensitized decomposition of methane and produce methyl radicals, CH_3.[5,19] The reaction of two methyl radicals would result in the production of ethane. This hypothesis will be tested by photolyzing mixtures of acetylene and methane at a wavelength that will not photolyze methane. Analysis of the gas products should establish how much the photosensitized decomposition of methane will increase the abundance of ethane in Titan's stratosphere. The same type of reaction mechanism can be used to describe the production of propane.

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Physical Characteristics of Titan[6]

Characteristic	Absolute Value	Relative to Earth
Surface Radius	2575 km	
Mass		2.2%
Surface Gravity	135 cm/sec^2	14%
Mean Density	1.88 g/cm^3	34%

	Saturn	Sun
Distance from Saturn	1.226 x 10^6 km	1.43 x 10^9 km
Orbital Period	15.95 day	30 years

Temperature	
Surface	94 K
Tropopause (42 km)	70 - 75 K
200 km altitude	170 K

Pressure	
Surface	1.5 bar
200 km altitude	1 mb

Table 1.1: The physical structure of Titan and it's relationship to the Earth, Saturn, and the Sun. The temperature profile of Titan is of particular interest. The atmospheric temperature minimum is at the tropopause and will restrict the contribution of surface gases to the stratosphere.

The Titanian Atmosphere[6]

(Equatorial Region)

Compound	Name	Abundance
Major Constituents		
N_2	Nitrogen	76 - 99%
Ar	Argon	0 - 21%
CH_4	Methane[2]	6%
H_2	Hydrogen	0.2 - 0.6%

Hydrocarbons (mixing ratios)

		Surface	Tropopause	Stratosphere
CH_4	Methane	$1.2x10^{-1}$	$3.0x10^{-2}$	$1-3x10^{-2}$
C_2H_6	Ethane	$4.0x10^{-5}$	$5.1x10^{-7}$	$2x10^{-5}$
C_2H_2	Acetylene	$8.0x10^{-7}$	$6.9x10^{-10}$	$2x10^{-6}$
C_2H_4	Ethylene	$1.9x10^{-4}$	$4.1x10^{-6}$	$4x10^{-7}$
C_3H_8	Propane	$4.8x10^{-7}$	$1.3x10^{-9}$	$2-4x10^{-6}$
C_4H_2	Diacetylene	$1.2x10^{-12}$	$7.4x10^{18}$	$10^{-7}-10^{-8}$

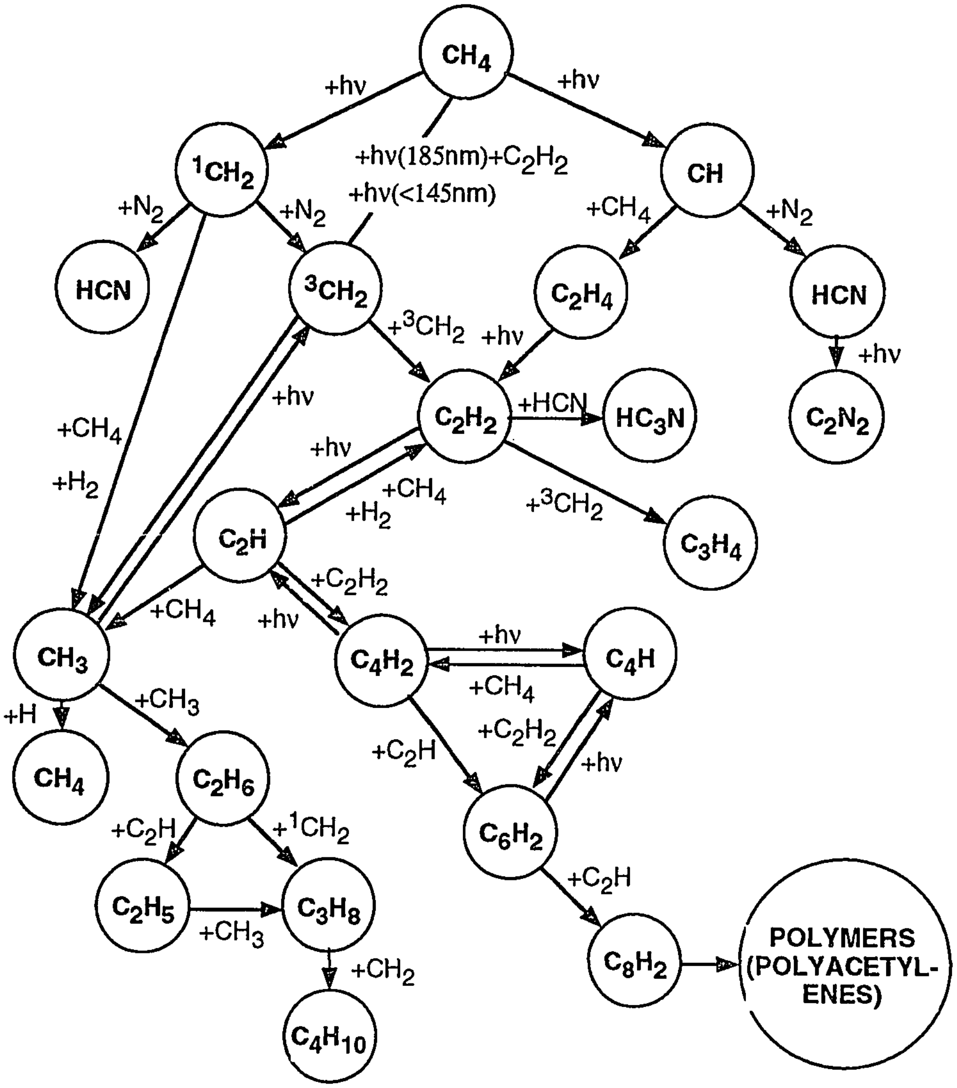
Compound	Name	Abundance
Nitriles		
HCN	Hydrogen Cyanide	0.16 ppm
HC_2CN	Cyanoacetylene	<0.002 ppm
C_2N_2	Cyanogen	<0.002 ppm
Oxygen Compounds		
CO	Carbon Monoxide	60 ppm
CO_2	Carbon Dioxide	0.01 ppm

Table 1.2: Titan's atmosphere contains a variety of hydrocarbons, nitriles and oxygen compounds. The mixing ratios of the hydrocarbons at different atmospheric regions shows that most gases were not limited by the tropopause temperature restrictions.

Photochemical Reactions

1. $CH_4 + hv \longrightarrow CH_3 + H$
2. $CH_4 + hv \longrightarrow {}^1CH_2 + H_2$
3. $CH_4 + hv \longrightarrow CH_2 + 2H$
4. $CH_4 + hv \longrightarrow CH + H + H_2$
5. $2CH_4 \longrightarrow C_2H_2 + 3H_2$
6. $2CH_4 \longrightarrow C_2H_2 + 4H + H_2$
7. $2CH_4 \longrightarrow C_2H_4 + 2H + H_2$
8. $2CH_4 \longrightarrow C_2H_4 + 4H$
9. $C_2H_2 + hv \longrightarrow C_2H + H$
10. $C_2H_2 + hv \longrightarrow C_2 + H_2$
11. $C_2H + C_2H_2 \longrightarrow C_4H_2 + H$
12. $C_2H + C_4H_2 \longrightarrow C_6H_2 + H$
13. $C_2H + C_6H_2 \longrightarrow C_8H_2 + H$
14. $C_2H + C_nH_2 \longrightarrow C_{n-2}H_2 + H$
15. $C_2H + CH_4 \rightarrow C_2H_2 + CH_3$
16. $C_2 + CH_4 \rightarrow C_2H + CH_3$
17. $CH_2 + CH_3 \rightarrow C_2H_5$
18. $C_4H_2 + hv \rightarrow C_4H + H$
19. $C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$
20. $C_4H + C_2H_6 \rightarrow C_4H_2 + C_2H_5$
21. $CH_3 + C_2H_5 \rightarrow C_3H_8$
22. $C_2 + H_2 \rightarrow C_2H + H$
23. $C_2H + H_2 \rightarrow C_2H_2 + H$
24. $C_2H + C_nH_m \rightarrow C_2H_2 + C_nH_{m-1}$
25. $C_4H + C_nH_m \rightarrow C_4H_2 + C_nH_{m-1}$
26. $C_4H + C_2H_2 \rightarrow C_6H_2 + H$
27. $C_4H + C_4H_2 \rightarrow C_8H_2 + H$
28. $C_6H_2 + hv \rightarrow C_6H + H$
29. $C_6H + C_nH_m \rightarrow C_6H_2 + C_nH_{m-1}$
30. $C_6H + C_2H_2 \rightarrow C_8H_2 + H$

Table 1.3: This is a short list of photochemical reactions believed to occur in Titan's Stratosphere that were discussed in this research.[5,20]



HYDROCARBON PHOTOCHEMISTRY ON TITAN

Figure 1.1: Schematic diagram of important hydrocarbon photochemical reactions, based on Strobel (1974), Allen *et al.* (1980), Yung *et al.* (1984), Yung (1987), and Mordaunt (1992).

Scattergood 5/93, Clegg 1/94

2. Experimental

2.1. General Procedures

Gas samples of acetylene and nitrogen were prepared in a photolysis cell and photolyzed at 185 nm for typically 1 hour. The samples were prepared by connecting the cell and a gas cylinder to the vacuum system and evacuating to at least 0.01 torr (10 microns of mercury). They were then purged at least 3 times, and filled with the needed pressure of gas. The cell was closed, the gas cylinder was changed, and the system was evacuated. The system was again purged 3 times while the cell was closed. The sample was added to the cell by over filling the vacuum system, opening the photolysis cell, filling the system and cell to the desired pressure plus the pressure of the gases already in the cell, and then quickly closing the cell. This was repeated for each gas added to the cell, beginning with the gas at the lowest pressure. The gases were used directly from the gas cylinders without further purification. The acetylene was Matheson purified grade and the nitrogen gas was Liquid Air purified grade. The sample was allowed to equilibrate for at least 20 minutes before sampling or photolysis.

The photolysis cell used in most of the experiments was a 3.0 x 22.0 cm glass cylinder. Each end of the cell was open and fitted with an O-ring. A Suprasil quartz window was clamped to the top of the cell and a glass cup was clamped to the bottom of the cell.

The samples were photolyzed by a low pressure mercury lamp that contains a few drops of mercury and 3 torr argon specially made by Opthos Instruments. A special sleeve was also purchased from Opthos Instruments that distributes the microwave energy to the entire lamp. The entire system was powered by a Kiva microwave generator. The lamp was lit by increasing the power to about 25 W and "tickling" the lamp with a tesla coil. It was allowed to warm up for at least 20 minutes before photolysis. The photolysis cell was raised on a lab jack to within 2mm of the lamp and held in place by a utility clamp. A sketch of the photolysis system discussed above is shown in Fig. 2.1.

The lamp flux is the number of photons emitted per second and was monitored to ensure that it stayed relatively constant for all of the experiments. In these experiments, acetylene is photolyzed at 185 nm. During each experiment, the lamp flux was measured by an Ultra-Violet Products, Inc. UVX radiometer. The radiometer sensor detects light at 254 nm and was clamped in a fixed position approximately 5 cm from the lamp. This allows for immediate indication of potential lamp problems, however direct measurements of the flux at 185 nm were performed by another method, ammonia actinometry. Two UV-vis spectrophotometry cells were filled with 4 torr Matheson electronic grade ammonia. The absorption spectrum between 215 and 219 nm was taken 5 times with a Cary 3 spectrophotometer before and after photolysis. The amount of ammonia photolyzed over a fixed amount of time, usually 600 sec., was dependant upon the lamp flux. A discussion as to how the lamp flux was calculated via ammonia actinometry is found in Appendix A.

The silica window was cleaned prior to each experiment. The photolysis of acetylene produces a thin yellow film on the silica window. This was cleaned with a small amount of a dichloromethane and methanol solution on a cotton swab.

Polyacetylene also builds up on the walls of the photolysis cell over a number of experiments. This could be partially removed with the dichloromethane methanol solution. For a thorough cleaning, the photolysis cell was placed in an oven at about 450°C overnight.

2.2. Laboratory Studies of Polyacetylene Aerosol Particles

The photolysis cell was filled with between 0.01 to 10 torr acetylene as discussed above. The sample was placed under the low pressure mercury lamp, as depicted in Fig. 2.1, and photolyzed for 1 hour. As the polyacetylene aerosol particles formed, they began to settle to the bottom of the photolysis cell. A helium-neon (HeNe) laser beam was directed through the photolysis cell to provide a visible check that aerosols were forming. As the polyacetylene aerosol particles settled out, they passed through and scattered the laser beam. However, it became increasingly difficult to view the laser beam at acetylene pressures less than 1 torr, due to the lower aerosol number density and to the presumably smaller size of the aerosol particles.

The polyacetylene aerosol particles were allowed to settle to the bottom of the photolysis cell overnight and collected on a 1.7 cm diameter Corning glass cover slip. The photolysis cell was opened the next day and the cover slip was removed using a forceps. The cover slip was glued with Ted Pella, Inc. oil based Colloidal Graphite to a 25 mm carbon planchet from the same company. The sample was sputter coated with either gold or platinum in an argon purged environment using a Polaron Instruments, Inc. Scanning Electron Microscope E5100 Coating Unit. The argon was Liquid Air purified grade. The sample remained in the vacuum for 2 minutes after coating to allow the temperature to increase and prevent condensation on the sample. The sample was then removed from the coater and taped to a stand and placed in a Hitachi L-4000 Scanning Electron Microscope (SEM).

A Polaroid camera attached to the SEM was used to take pictures of the aerosol particles typically at 10K magnification. Depending on the initial acetylene pressure, 10 to 20 pictures were taken, each containing at least 10 aerosols particles. The number of aerosols in each picture decreased with decreasing acetylene pressure. At acetylene pressures less than 1 torr, the magnification was sometimes decreased to 5K in order to get more aerosols in each picture and maintain a good statistical sample.

Finally, the pictures were treated with a protecting film and the aerosols were measured using the same 14 cm ruler in all of the experiments. The scale after magnification was typically 1 mm equals 0.1 micron. As many individual particles as possible were measured to the nearest 1 mm and the number of particles per aggregate was recorded. In some cases, particles couldn't be measured because most of the particle was covered by another particle. However, the percent of total aerosols measured was typically greater than 85% of the total particles observed in the pictures.

2.3. Total Pressure Dependence on the Overall Rate of Aerosol Appearance

The photolysis cell was filled with 10 torr acetylene and between 0 and 450 torr nitrogen as discussed in section 2.1. The photolysis cell was placed under the lamp and shielded from the lamp light while the observer's eyes adjusted to the dark for 10 minutes to become more sensitive to the laser beam. The laser beam was directed through the cell at as close to the same position relative to the top of the cell and the lamp as possible. The distance from the top of the cell and the laser beam was approximately 2.70 cm. This was important because the photolysis and formation of the aerosols were accomplished within the first couple centimeters from the top of the cell. Eventually, the aerosols settled and passed through the laser beam. The time it took for the aerosols to scatter the beam enough to become visible at a forward angle was determined. The forward scattering of the laser was chosen because the beam first becomes visible at forward angles as per scattering theory. Once the beam was detected, the experiment was completed and the procedures were repeated for a number of different nitrogen pressures.

2.4. Gas Chromatographic Studies of the Photolysis of Acetylene

Gas samples of acetylene, methane and nitrogen were prepared as discussed in section 2.1. Control samples containing acetylene and nitrogen were also prepared in the same manner. Three extractions of each of the gas samples were analyzed by a Perkin-Elmer 900 Flame Ionization Detector Gas Chromatograph (FID GC) with a Waters and Associates, Inc. Phenylisocyanate on Porocil C packed column before and after photolysis. The extractions were accomplished by connecting the photolysis cell to an injection port made up of two loops, 0.257 and 0.269 ml. At any given time, one of the loops would be open to a belt driven vacuum pump and the photolysis cell. The other loop would be open to the column and carrier gas, Scotty Specialty Gases 99.999% helium. The FID detector used NASA Ames Research Center store stock compressed air and hydrogen from a Milton Roy hydrogen generator.

Once the photolysis cell was attached to the injection port, the injection port was pumped down for at least 4 minutes to approximately 100 torr with a mechanical vacuum pump coupled with a liquid nitrogen trap. In order to extract a sample, the loop was closed off from the pump and the sample was expanded into the loop for 30 seconds. The photolysis cell was closed and the sample was injected into the GC. The second loop would be pumped until the injected sample was completed. The injection handle was switched back to the original loop so that the same loop was always used and the procedures were repeated.

The gases that were quantitatively measured in these experiments were methane, ethane, ethylene, propane, and acetylene. Before and after each experiment, Matheson Certified Calibration Gas Standard samples containing 0.20% methane and acetylene and 0.21% ethane, ethylene, and propane, with a helium balance, were injected from a 250 ml round bottom flask fitted with a stopcock. The standard flask was filled with a known pressure of standard, approximately 760 torr. At most, 15 samples of the standard would be taken before it would be refilled, to limit the errors associated with the expansions. Other gases were also qualitatively identified from the chromatograph using Scotty Brand Gases.

Peak areas of the chromatograph were calculated with a Hewlett-Packard 3394A integrator. The standards were analyzed to determine the molar response (MR) in peak area counts per nanomole, which is simply the slope of the calibration curve. Calibration curves were done for methane and acetylene to verify that the curves were indeed linear and are shown in

Fig. 2.2a and 2.2b. However, the MR for a given experiment was determined from the standard samples taken that day.

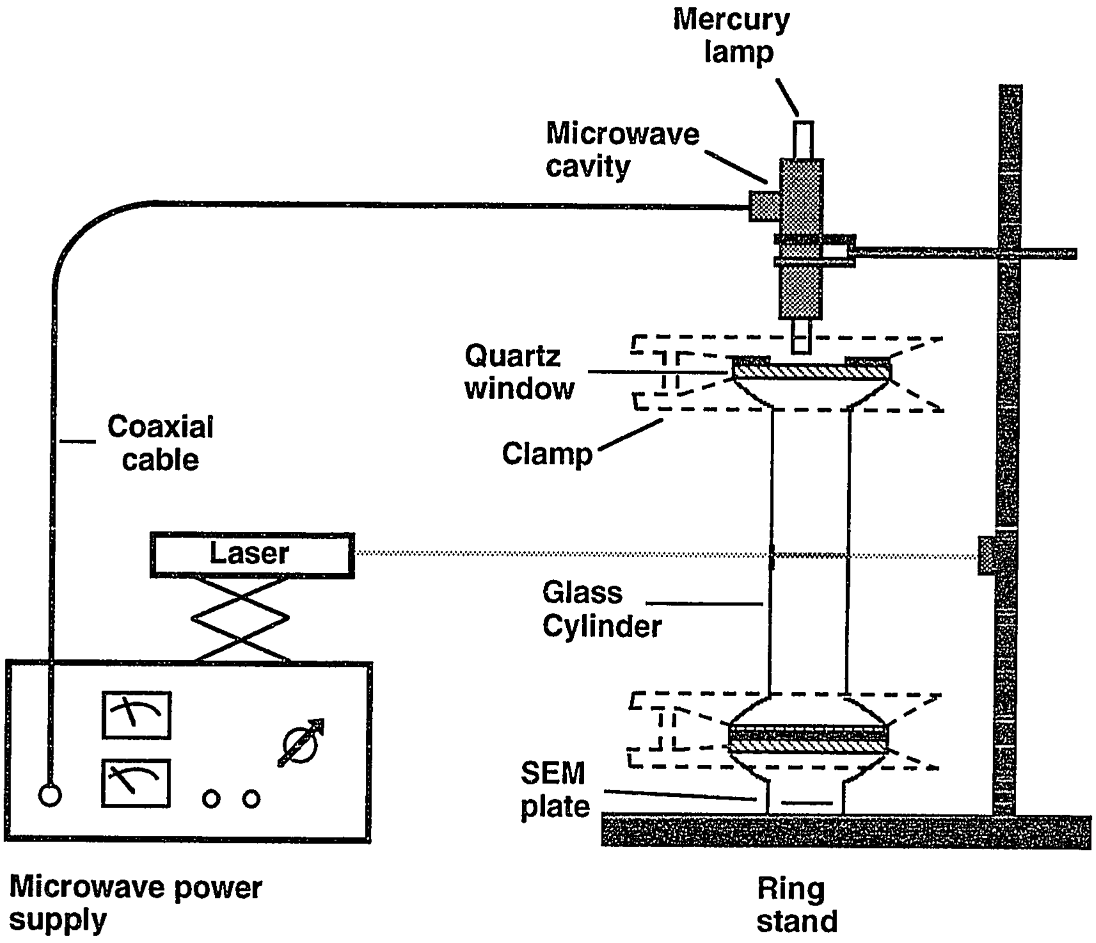


Figure 2.1: A diagram of the photolysis system used to photolyze the gas samples. The low pressure mercury lamp photolyzed the samples primarily at 185 nm. The Helium Neon laser was directed through the photolysis cell and was scattered by the polyacetylene aerosols. The polyacetylene aerosol collection plate was at the bottom of the photolysis cell.

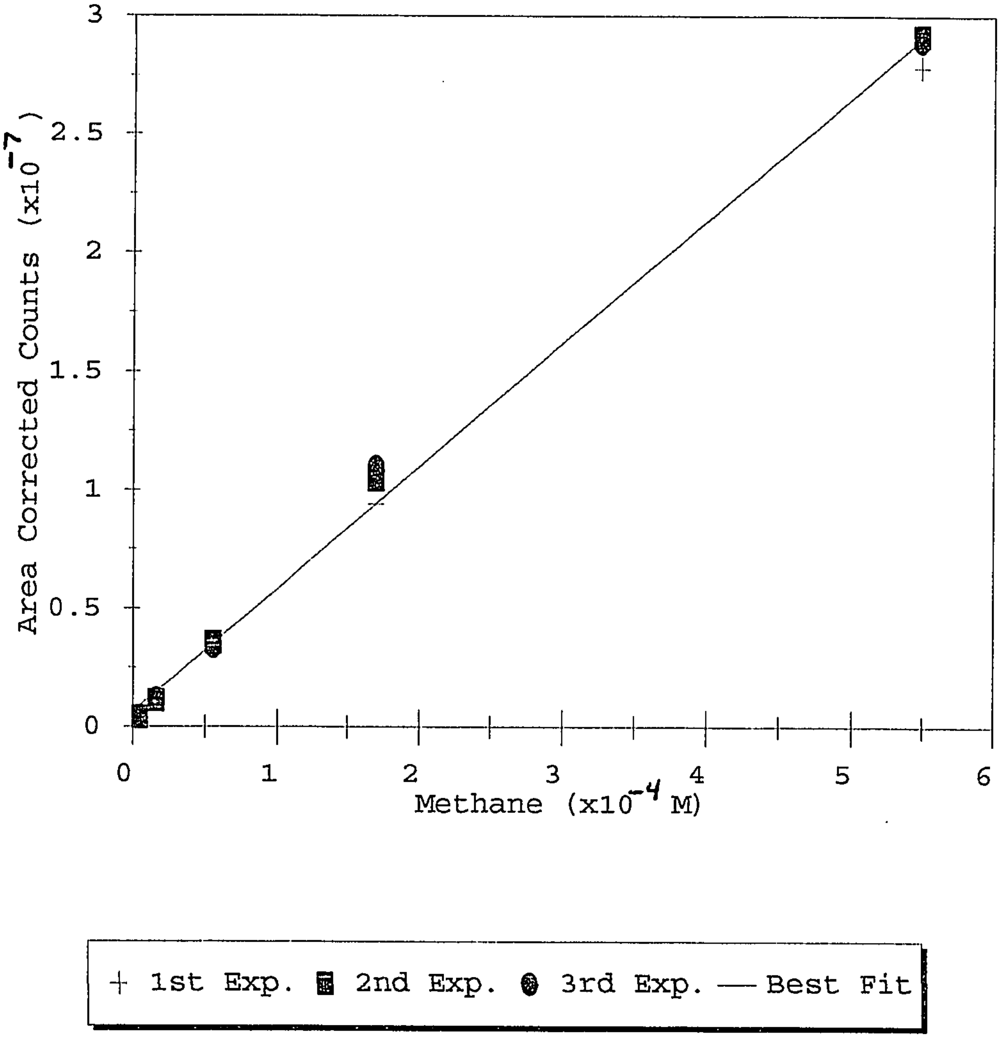


Fig. 2.2a: Gas chromatographic calibration curve for methane. It was done to verify that the calibration curves were indeed linear.

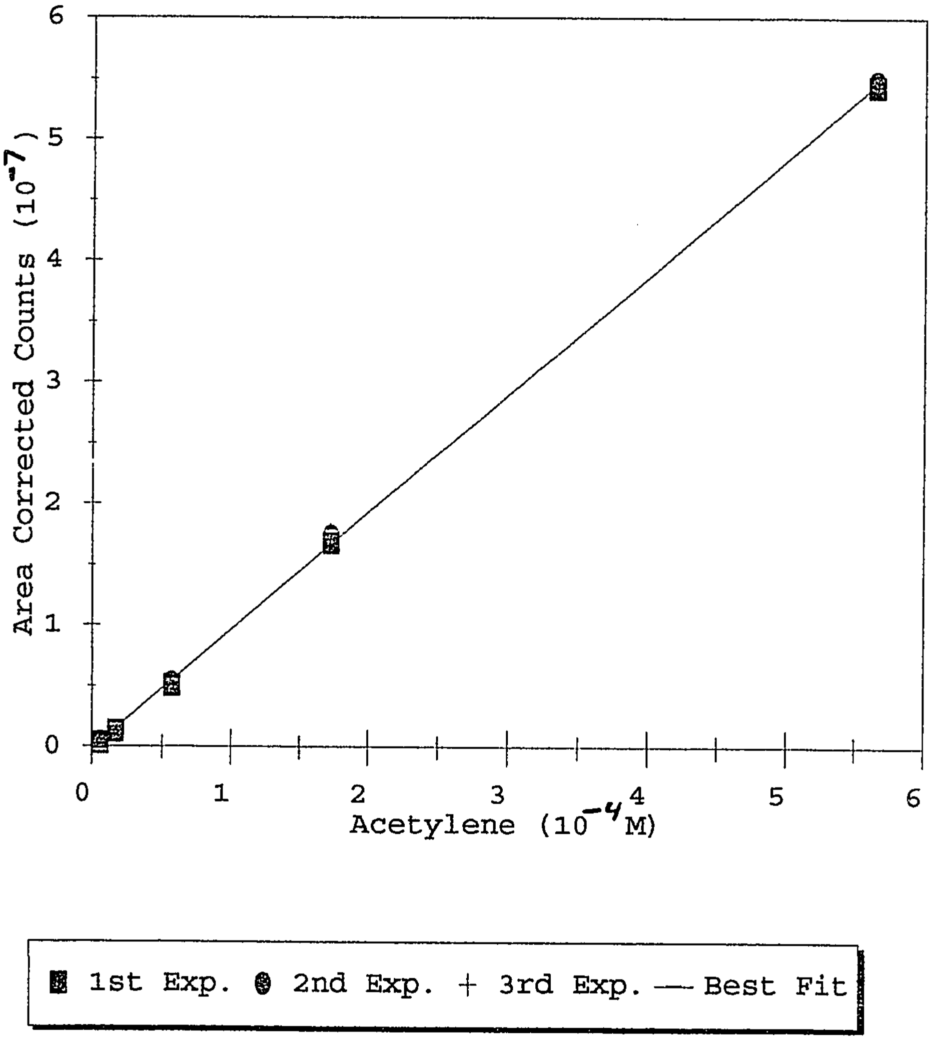


Fig. 2.2b: Gas chromatographic calibration curve for acetylene. It was done to verify that the calibration curves were indeed linear.

3. Results and Discussion

3.1 Laboratory Studies of Polyacetylene Aerosol Particles

The photolysis of acetylene is known to produce polyacetylene* aerosol particles. Samples of between 0.01 and 10 torr acetylene and approximately 60 torr nitrogen were photolyzed at 185 nm for 1 hour. The flux of the low pressure mercury lamp at 185 nm for these experiments was $5.12\times10^{15} \pm 1.89\times10^{15}$ photons/second. The resulting polyacetylene aerosol particles were allowed to settle on a glass cover slip and imaged by scanning electron microscopy (SEM). The diameter of as many individual particles as possible was measured with a ruler from the Polaroid pictures. Most of the pictures were imaged at a 10K magnification. However, at acetylene pressures lower than 1 torr, fewer particles were observed. To increase the number of particles in each picture, the magnification was decreased to 5K.

Polaroid pictures of what the polyacetylene aerosol

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*Aerosols produced from the photolysis of acetylene are called polyacetylene aerosol particles. However, the actual composition of the aerosols is unknown. It is more likely that they are a mixture of polymer chains of acetylene, ethylene and hydrogen cyanide.

particles look like are shown in Fig. 3.1 as well as in Scattergood *et al.* (1992).[1] The aerosol particles were spherical in shape and apparently amorphous, a result in agreement with previously reported observations.[1] Between 50 and 200 particles were measured in each experiment, depending on the acetylene pressure. As the acetylene pressure decreased, there was less acetylene to produce the polyacetylene aerosol particles and therefore fewer particles were observed. A plot of the size distribution of the aerosol particles was generally gaussian or log normal with particles ranging from 0.1 to approximately 1.2 um in diameter, as is shown in Fig. 3.2. Particles larger than 1.2 um in diameter were occasionally observed. The reason that polyacetylene aerosol particles smaller than 0.1 um in diameter were not observed was due presumably to the collection method and not the SEM detection limit. Duke Scientific Certified Polystyrene Spheres were easily imaged as small as 0.04 um in diameter.

The mean particle radius and standard deviation of the polyacetylene aerosol particles were calculated for acetylene pressures ranging from 0.01 to 10 torr. A plot of the mean particle radius as a function of the acetylene pressure is shown in Fig. 3.3. The mean particle radius increased from 0.2 to 0.4 um as the acetylene pressure increased from 0.2 to 10 torr.[2] However, the mean particle radius of the polyacetylene aerosol particles increased to 0.6 um as the acetylene pressure decreased from 0.1 and 0.01 torr. The reason for this increase in size is probably due to the sampling method. It is believed that the aerosols need to reach a certain size before they fall out onto the cover slip. Many of the smaller particles may not reach the cover slip because of diffusion of the particles to the walls of the cell or with other particles resulting in the production of larger particles. Very few particles were observed in these lower pressure experiments and the statistical validity of the data is suspect.

The polyacetylene aerosol particles were observed to be very adhesive and aggregates of the particles range in number from 2 to 17 particles per aggregate, a result previously observed.[1] The adhesive property of these aerosols can be observed in the pictures in Fig. 3.1. Some of the aerosols appear to be stacked on top of each other and a side view of these particles, as viewed in Scattergood *et al.* (1992), also verifies this conclusion.[1] From a plot of the number of particles per aggregate versus the frequency, Fig. 3.4, most of the particles were observed in aggregates. However, the single most frequent categories contained either single particles or aggregates of 2 particles.

Analysis of Voyager observations led to the conclusion that the radius of the aerosol particles in the main haze layer were between 0.25 and 0.5 um with particles as small as 0.02um observed in the outer most haze layers.[3-5] The polyacetylene aerosol particles produced in the laboratory are in good agreement with these Voyager observations, even though the smaller particles were not observed in these experiments. An explanation for the discrepancy of particle sizes has been the presence of non-spherical particles. Analysis of the Voyager data assumed that only spherical particles were present.[3] The individual particles observed in the simulations were consistently spherical; however, most of the particles were in aggregates that consequently behave optically as non-spherical scatters.

A model by Cabane *et al.* (1992) investigated the production of the aerosols as a function of acetylene pressure. It was determined from the model that there are two stages of aerosol growth.[6] The first stage occurs at very high altitudes, between 350 and 450 km, where there is a relatively small amount of acetylene present.[6] The particles produced were called "monomers," spherical particles of approximately a 0.06 um radius.[6,7] Once formed, the aerosols fall in altitude entering areas of increased acetylene pressure and aerosol density.[6] As the aerosols collide with other aerosol particles, they begin to aggregate and produce larger particles. From the model, it was determined that approximately 10 monomers per aggregate would be consistent with the Voyager observations and analysis of non-spherical particles.[6] However, this was not observed in the laboratory simulations. Even though most of the particles were observed as aggregates, the frequency decreased as the particles per aggregate increased.

The main uncertainty of the Cabane *et al.* (1992) model is the uncertainty in the acetylene pressure as a function of the altitude, a parameter that should be determined by Huygens Probe.[6] The results of these experiments are in general agreement with the Cabane *et al.* (1992) model. The particle size distribution dependence on the acetylene pressure was observed. Given the extreme temperature, pressure, and gravitational differences between Titan and the laboratory, these results are encouraging. The growth and collision lifetime of the laboratory produced particles is one hour, where the aerosols on Titan presumably grow and settle over a much longer lifetime. The agreement between Titan observations and laboratory simulations could mean that the laboratory produced aerosol particle is a reasonable analogue to those found in the Titan haze layers.

3.2 Total Pressure Dependence on the Overall Rate of Aerosol Appearance

Samples of 10 torr acetylene and between 0 and 450 torr nitrogen were photolyzed at 185 nm. The resulting polyacetylene aerosol size and number density were sufficient to see a cloud form at the top of the photolysis cell and descend down the middle of the cell. The time it took for the aerosols to pass through and scatter the HeNe laser beam was measured. The plot of the time it took for the beam to become visible to the human eye in a forward scattering direction as a function of the total pressure is shown in Fig. 3.5. The flux of the low pressure mercury lamp at 185 nm for these experiments was $5.12 \times 10^{15} \pm 1.89 \times 10^{15}$ $h\nu$/second.

As the total pressure increased from 0 to approximately 60 torr, the time it took for the beam to become visible decreased from 10.5 to 1 minute. There was little or no change in the time it took for the beam to became visible at total pressures greater than 60 torr. Therefore, it appears that at total pressures less than 60 torr, the overall rate of aerosol appearance is dependent on the total pressure. The overall rate of aerosol appearance is dependent on some other step at total pressures greater than 60. Perhaps, the production of the polyacetylene aerosols requires a collision partner. Reaction (21) of Table 1.3 is an example of a reaction that requires a collision partner.

$$CH_3 + C_2H_5 + M \dashrightarrow C_3H_8 + M \qquad (21)^8$$

On Titan, the abundance of nitrogen and the suggested presence of argon might also act as effective collision partners and enhance the production of the aerosols. However, where in the overall production process is the collision partner necessary is unknown. The effect of the total pressure on the size and number density of the resulting aerosol particles is also unknown. The total pressure in the experiments in the previous section was approximately 60 torr, most of which was nitrogen. Therefore, it seems that at this total pressure, the production of aerosols was maximized.

In order for the particles to scatter the laser beam enough to become visible, the particles need to either reach a certain size, number density, or combination of the two. Initially, 1 torr acetylene samples were tested but the results were not consistent. This was probably due to the decreased scattering due to smaller particle size or number density. Unfortunately, the data doesn't address changes as to the aerosol size or density and an *in situ* method of determining the particle size distribution and density is needed.

3.3. Gas Chromatographic Studies of the Photolysis of Acetylene

The photolysis of acetylene produces methane, ethane, ethylene, and propane along with many other hydrocarbons including diacetylene. Quantitative analysis of the head space gas for all of these hydrocarbons, except diacetylene, was measured by gas chromatography (GC). Calibration standard extractions were measured before and after each series of experiments each day and the molar response was calculated by equation 1:

$$MR_{STD} = \frac{AC_{STD}}{ER^{i}} \tag{1}$$

where MR_{STD} and ER^i are the molar response and the ith expansion of the standard, respectively.

Samples of acetylene and nitrogen (C_2H_2/N_2) were photolyzed for 1 hour to determine the concentration of the above analytes produced by the photolysis of acetylene. The percent acetylene, by weight, used to produce each of the products was also determined. The results served as a control in determining the effect excess methane has on the products of the photolysis of acetylene. Three extractions of each sample were taken before and after the photolysis. The moles of analyte were calculated by equation 2:

$$n_i = \frac{AC_{sample}}{MR_{STD.avg.}} \tag{2}$$

where AC_{sample} and $MR_{STD.avg}$ are the area counts of the sample and average molar response of the standard, respectively. The derivation of equations 1 and 2 can be found in Appendix B. The lamp flux for the results reported in this section was $3.43 \times 10^{-15} \pm 1.27 \times 10^{-15}$ $h\nu$/second.

Between 40% and 60% of the acetylene from both C_2H_2/N_2 and $C_2H_2/CH_4/N_2$ samples was decomposed in 1 hour, depending on the initial acetylene pressure and lamp flux. The concentration of acetylene photolyzed increased linearly as the acetylene pressure increased from 0.1 to 10 torr, as shown in Fig. 3.6. Therefore, the addition of methane did not change the total amount of acetylene photolyzed.

Ethylene was the most abundant of the observed products in both the C_2H_2/N_2 and $C_2H_2/CH_4/N_2$ samples. There was little or no change in the amount of ethylene produced with or without methane added to the sample, as shown in Fig. 3.7. The production of ethylene accounts for 1.68% (± 0.45%) of the photolyzed acetylene. However, the observed ethylene production was a somewhat misleading result. Ethylene also photolyzes at 185 nm.[8] When the photolysis is continued for more than an hour, the ethylene concentration decreased as shown in Fig. 3.8. Therefore, production rate of ethylene in the first hour was greater than the rate of photolysis, and the net result was an increased concentration of ethylene. As the acetylene concentration decreased, the ethylene production rate decreased. After 1 hour, the production rate of ethylene was slower than the rate of photolysis and the net result was a decrease in the ethylene concentration. All of the ethylene was consumed in approximately 3 hours.

The amount of methane produced from the photolysis of C_2H_2/N_2 accounts for approximately 0.36% (±0.19%) of the photolyzed acetylene. The amount of methane produced increased as the acetylene pressure increased, as shown in Fig. 3.9. However, when the same amount of acetylene was photolyzed and between 0.1 and 10 torr methane was added, the amount of methane remaining in the sample decreased. The observed decrease in methane could not be due to the photolysis of methane at 185 nm because methane doesn't photolyze at wavelengths greater than 145 nm.[8] Therefore, any changes in methane was due to other reactions. The decreased methane concentration was dependant on the initial methane pressure and independent of the initial acetylene pressure, as observed by Takita *et al.* (1968). That is, the amount of methane consumed increased as the initial methane pressure increased, as shown in Fig. 3.10. For each of the methane pressures tested, a range of acetylene pressures were used and there was no change in the amount of methane consumed at the different acetylene pressures. Finally, the amount of methane decomposed was on the order of 10^{-5} M. Therefore, if the catalytic decomposition of methane by the photolysis of acetylene results in the production of ethane as suggested, then the decomposition of methane in these experiments should be accompanied by an increased ethane production.

The ethane produced by the photolysis of C_2H_2/N_2 accounts for approximately 0.71% (± 0.37%) of the photolyzed acetylene. It has been suggested that the catalytic decomposition of methane by the photolysis of acetylene would result in an increased ethane mixing ratio in Titan's stratosphere.[6] When acetylene was photolyzed at 185 nm, it produced 2 intermediates:

$$C_2H_2 + h\nu \dashrightarrow C_2H + H \qquad (9)^{8}$$

$$C_2H_2 + h\nu \dashrightarrow C_2 + H_2 \qquad (10)^{8}$$

The photosensitized decomposition of methane by these intermediates produced methyl radicals.[8,13]

$$C_2H + CH_4 \dashrightarrow C_2H_2 + CH_3 \qquad (15)^{8,13}$$

$$C_2 + CH_4 \dashrightarrow C_2H + CH_3 \qquad (16)^{8}$$

The reaction of 2 methyl radicals would result in the production of ethane.[8,13]

$$CH_3 + CH_3 \dashrightarrow C_2H_6 \qquad (17)^{8,13}$$

Therefore, an increase in the ethane concentration should be observed in the samples where methane was added.

A comparison of the concentration of ethane produced with or without the addition of methane determined that there was no increase in the ethane produced, as shown in Fig. 3.11, in contrast to previous results.[13] The concentration of ethane produced was on the order of 10^{-7} M, two orders of magnitude less than the amount of methane decomposed. Therefore, some increase in the amount of ethane should have been observed in the samples containing methane. Therefore, the catalytic decomposition of methane by the photolysis of acetylene does not produce any more ethane than simply the photolysis of acetylene alone.[9-11]

The increased ethane mixing ratio in Titan's stratosphere might be explained, in part, by the findings of Mordaunt *et al.* (1992), where the photolysis of methane, similar to the work of Takita *et al.* (1968), was reexamined.[12] Their results determined that methyl radicals are the primary intermediates in the photolysis of methane, a result in contrast to the observations of Takita *et al.* (1968).[13] Therefore, it appears that the simple photolysis of methane may, in part, account for the increased ethane concentration in the stratosphere of Titan. The photolysis of acetylene and ethylene also produce ethane and therefore will contribute to the accumulation of ethane.

Finally, the amount of propane produced by the photolysis of C_2H_2/N_2 accounts for 0.36% (±0.28%) of the photolyzed acetylene. The same type of reaction mechanism can be used to explain the increased mixing ratio of propane in Titan's stratosphere. It has been suggested that an increased amount of propane would be produced by the photosensitized decomposition of methane and ethane by the photolysis of acetylene and diacetylene.[8] The photolysis of acetylene and diacetylene produces the following intermediates:

$$C_2H_2 + h\nu \dashrightarrow C_2H + H \qquad (9)^{8,13}$$

$$C_2H_2 + h\nu \dashrightarrow C_2 + H_2 \qquad (10)^{8}$$

$$C_4H_2 + h\nu \dashrightarrow C_4H + H \qquad (18)^{8}$$

These intermediates will cause photosensitized decomposition of ethane and produce ethyl radicals (C_2H_5).

$$C_2H + C_2H_6 \dashrightarrow C_2H_2 + C_2H_5 \qquad (19)^{8}$$

$$C_4H + C_2H_6 \dashrightarrow C_4H_2 + C_2H_5 \qquad (20)^{8}$$

The reaction of a methyl radical with an ethyl radical would produce propane.

$$CH_3 + C_2H_6 + M \dashrightarrow C_3H_8 + M \qquad (21)^{8}$$

There was little or no change in the amount of propane produced with or without methane added to the sample, analogous to the ethane results. The concentration of propane produced in both samples was on the order of 10^{-8} M propane, as shown in Fig. 3.12, which is three orders of magnitude less than the amount of methane decomposed. However, these results do not conclusively discount this process. The production of propane also depends on photosensitized decomposition of ethane to produce the ethyl radical (C_2H_5) intermediate. In these experiments, the only source of ethane was that produced by the photolysis of acetylene and it is unlikely that the ethane concentration ever become large enough to substantially increase the amount of propane produced. However, this does show that the lack of an increase in ethane was not the result of an increased propane concentration.

The production of these five hydrocarbons accounts for approximately 3.11% of the total photolyzed acetylene. Other products were also observed in this work and in the literature, including butane. If the total amount of the other gases produced was less than the gases quantitatively observed in these experiments, then more than 90% of the acetylene goes to the production of the polyacetylene aerosols. This indicates that the photolysis of acetylene is an efficient aerosol producing reactant.

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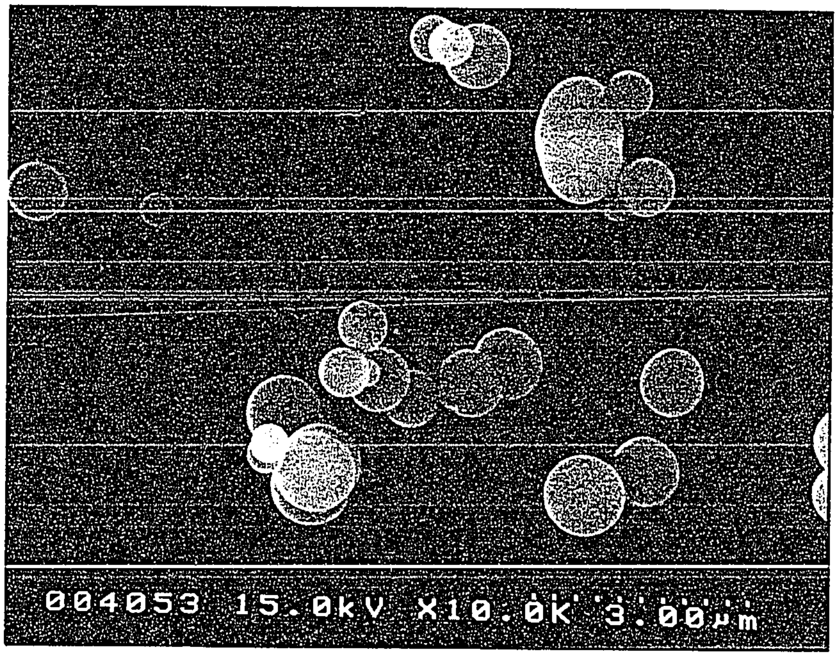

Fig. 3.1: An example of what the polyacetylene aerosol particles look like. These were produced from the photolysis of torr acetylene and 60 torr nitrogen for 1 hour at 185 nm. The individual particles are typically spherical and apparently amorphous. The adhesive property of the aerosols is also apparent by the number of aggregates observed.

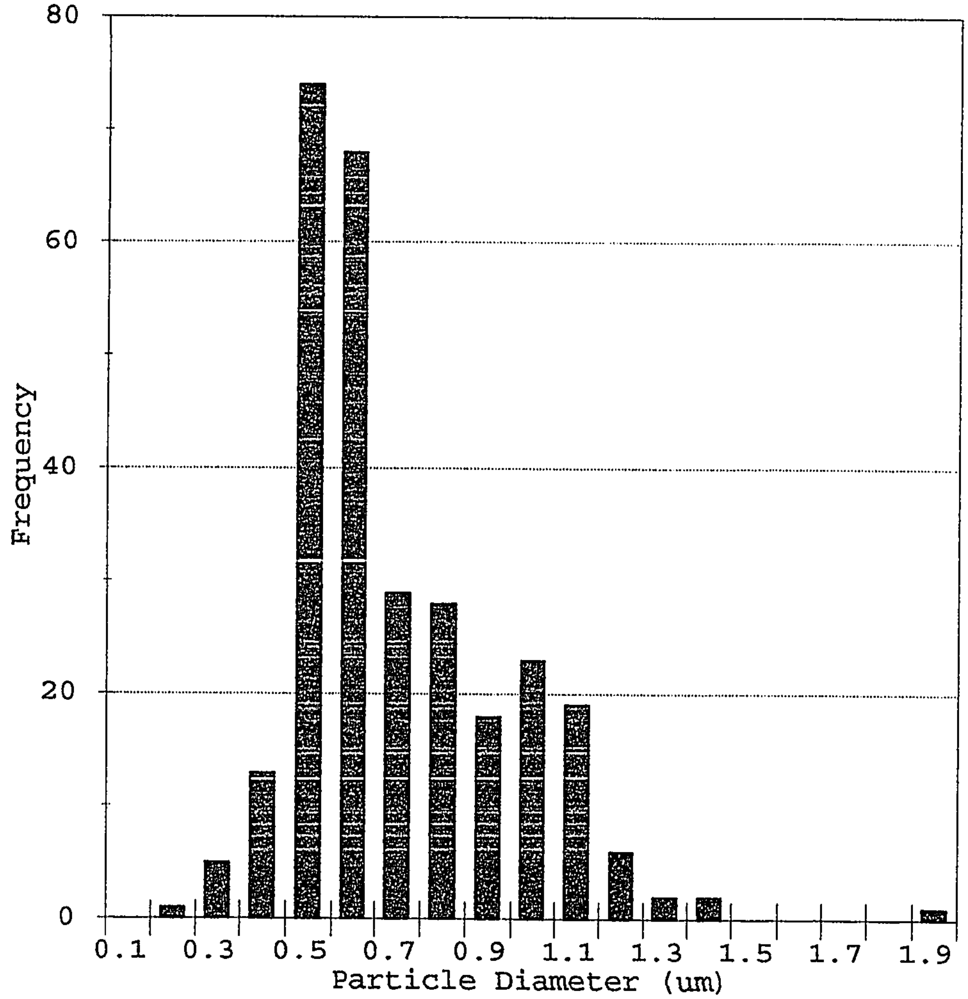

Fig. 3.2: The size distribution of polyacetylene aerosol particles produced by the photolysis of 10.24 torr acetylene and 60 torr nitrogen for 1 hour at 185 nm.

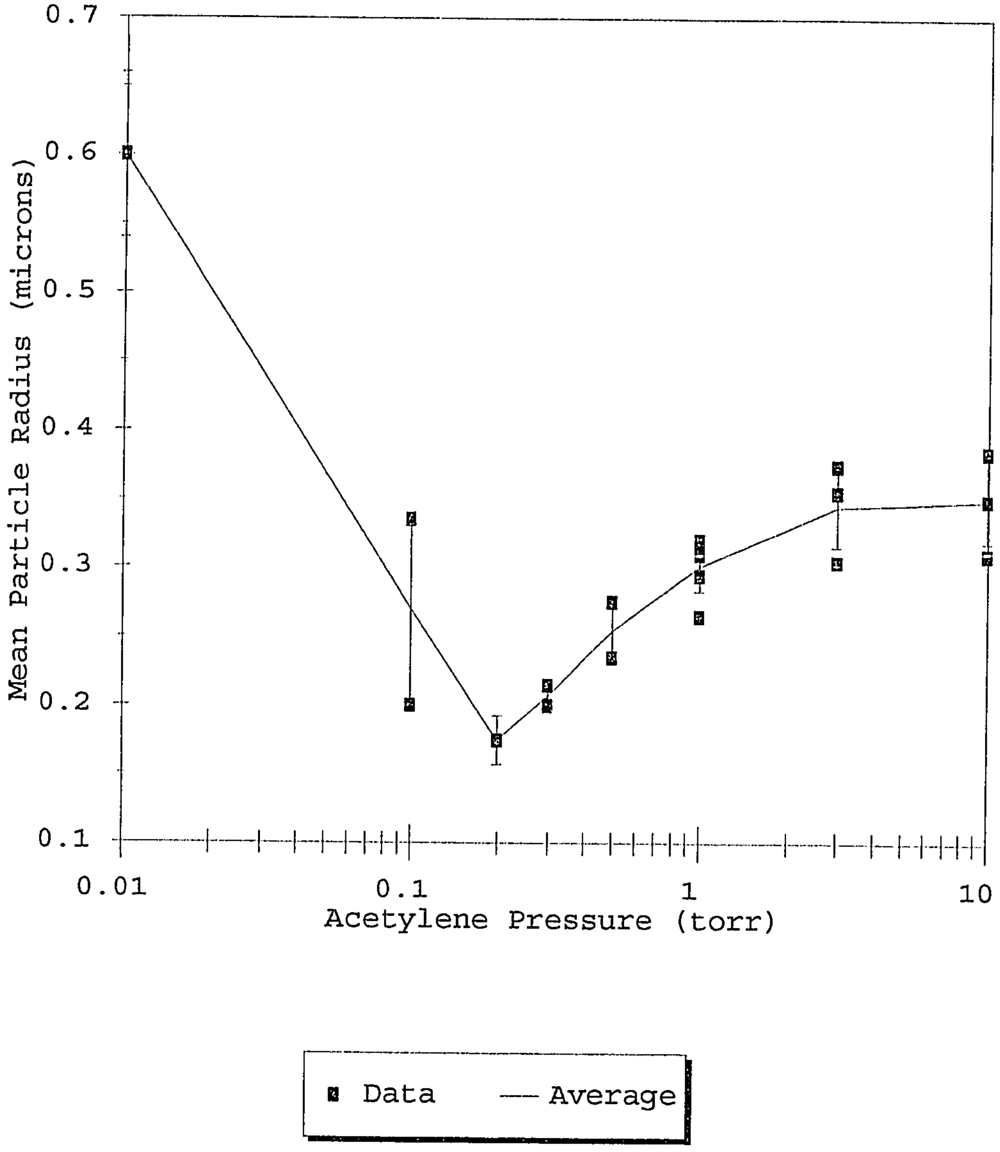

Fig. 3.3: The mean particle radius and standard deviations were calculated and plot against the acetylene pressure. The pressure dependence on the mean particle radius is observed.

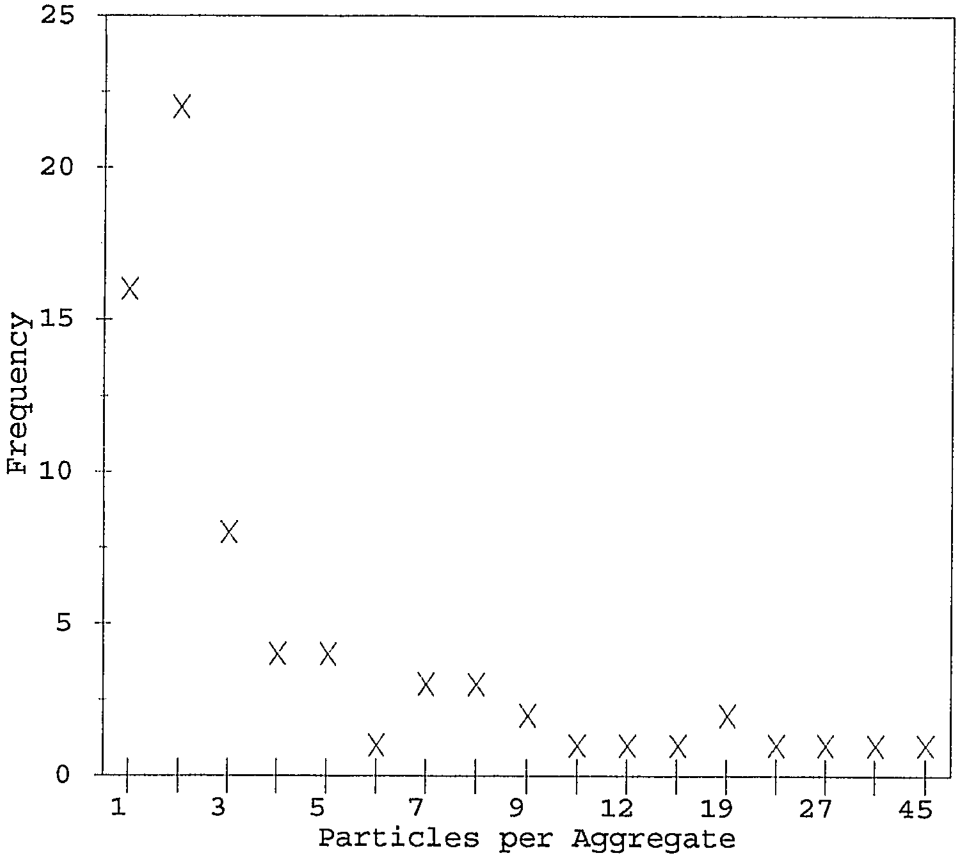

Fig. 3.4: The number of particle per aggregate vs. frequency. This shows that most of the particles are in aggregates due to their adhesive properties. The most frequent category was typically either single particles or aggregates of two particles.

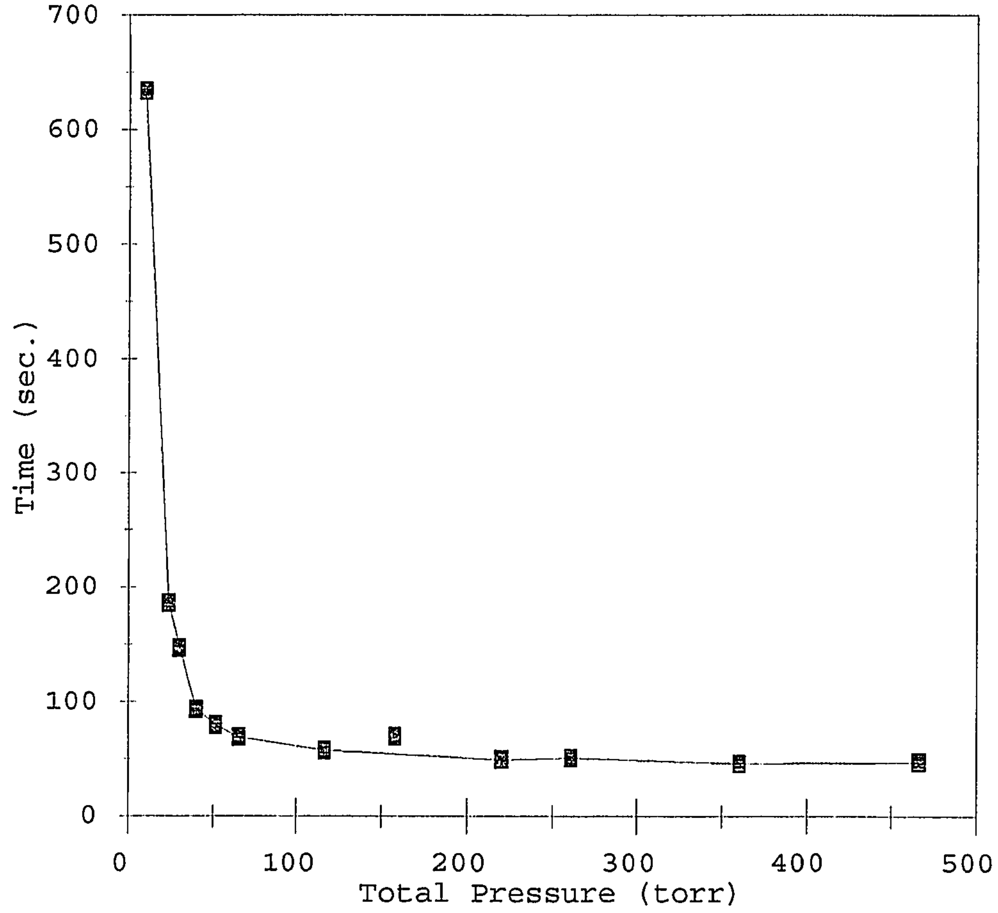

Fig. 3.5: The time it took for the HeNe laser beam to become scattered in a forward direction by the settling aerosol particles was measured. As the nitrogen pressure increased from 0 to 50 torr, the time rapidly decreased. There was little change in the time at nitrogen pressures greater than 50 torr.

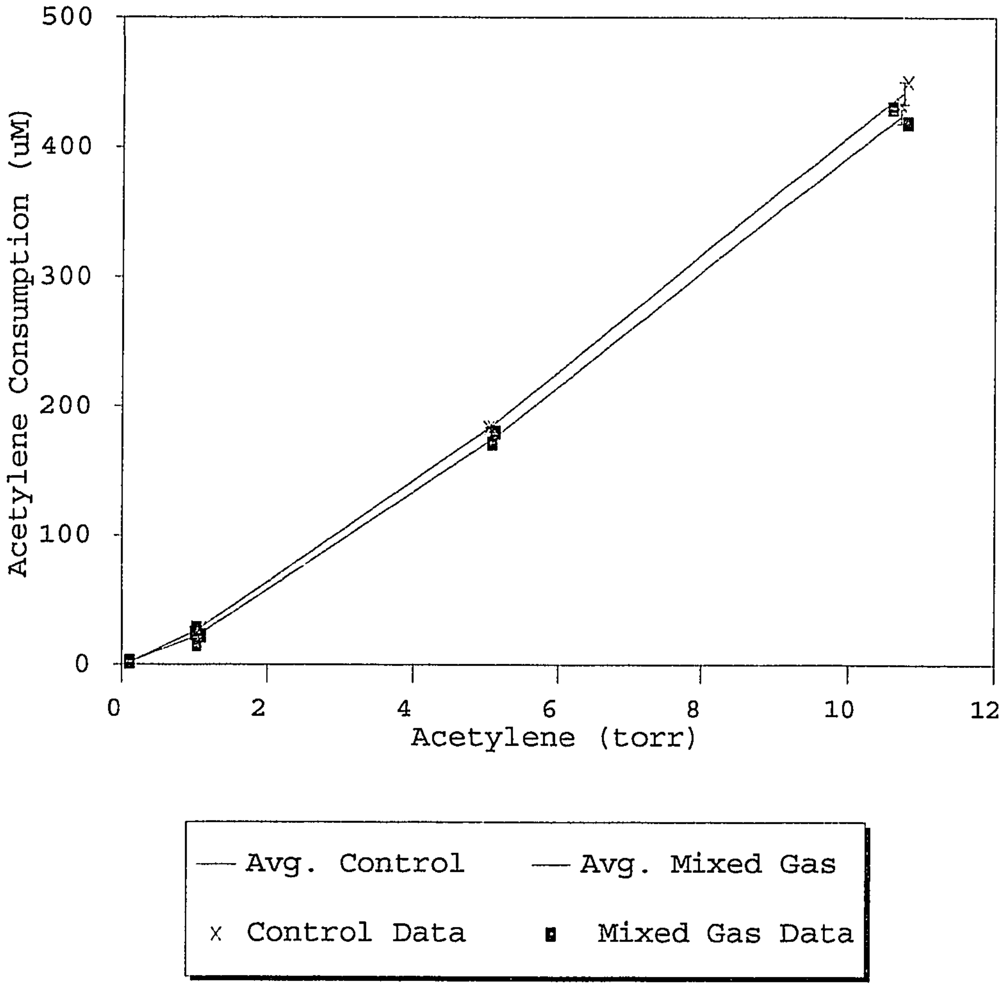

Fig. 3.6: The amount of acetylene photolyzed in samples of acetylene, methane and nitrogen compared to the control. The addition of methane to the photolysis of acetylene didn't decrease the amount of acetylene that was photolyzed.

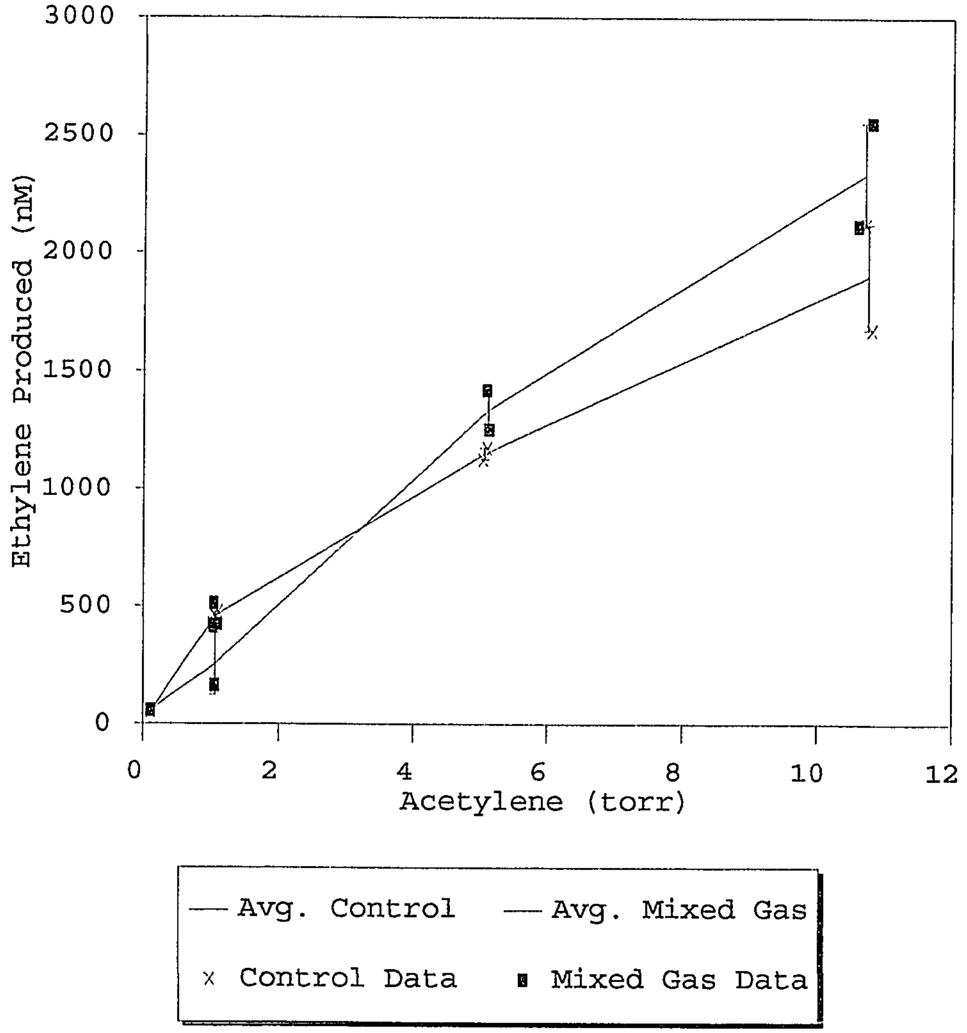

Fig. 3.7: The production of ethylene from the photolysis of acetylene, methane, and nitrogen compared to the control at 185 nm for 1 hour. The amount of ethylene produced didn't change when methane was added in the sample.

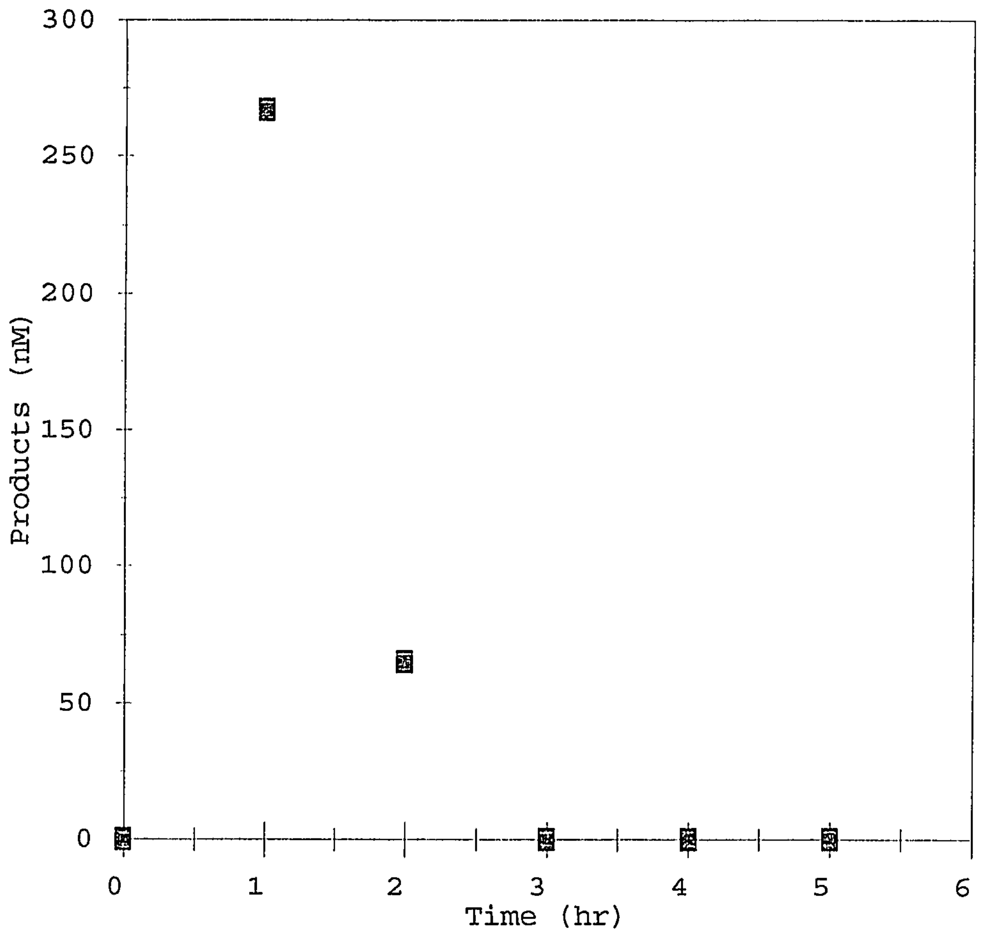

Fig. 3.8: This plot shows the production and decomposition of ethylene after 5 hours of acetylene and ethylene photochemistry.

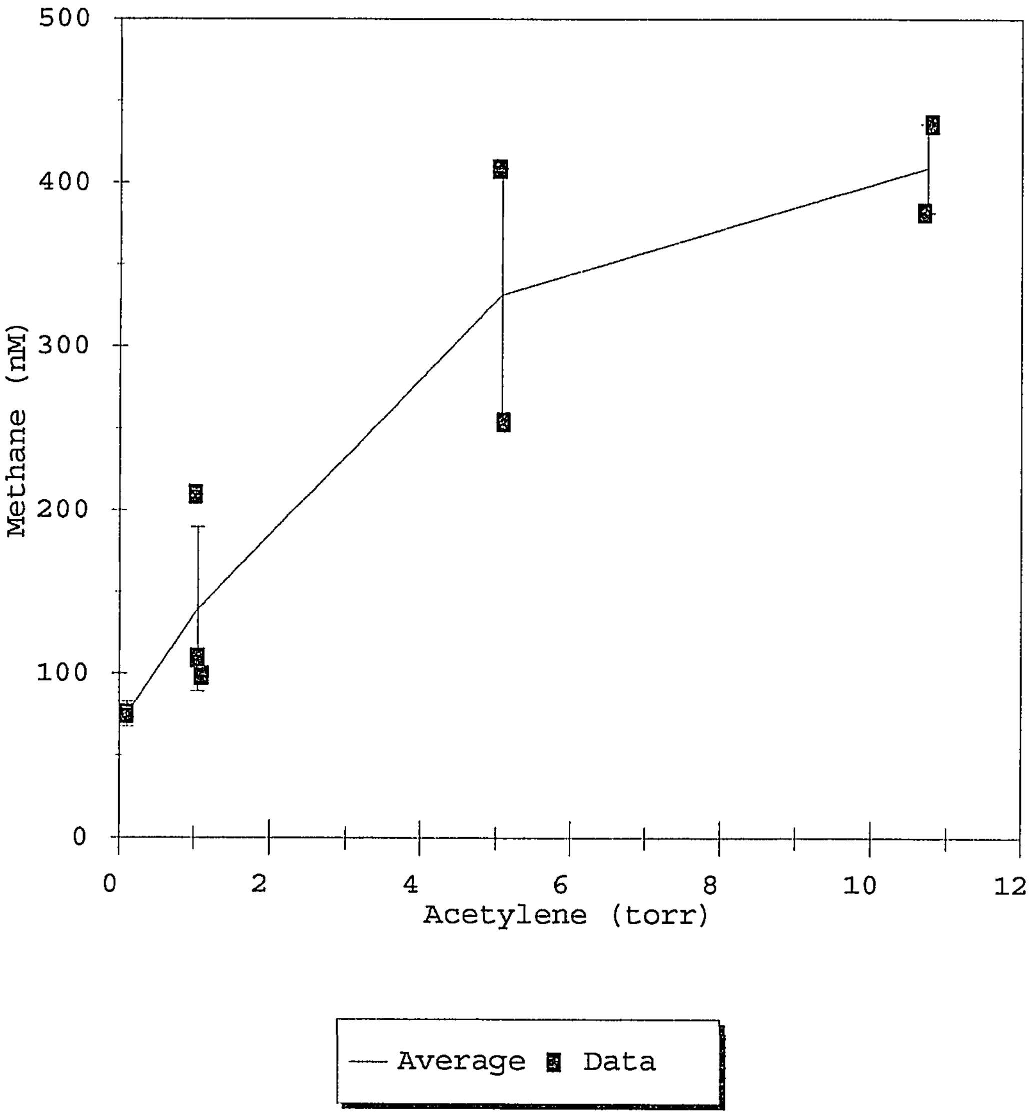

Fig. 3.9: The production of methane in samples of just acetylene and nitrogen (C_2H_2/N_2) as a function of acetylene pressure. The concentration of methane produced from the photolysis of acetylene at 185 nm for 1 hour is on the order of 10^{-7}M.

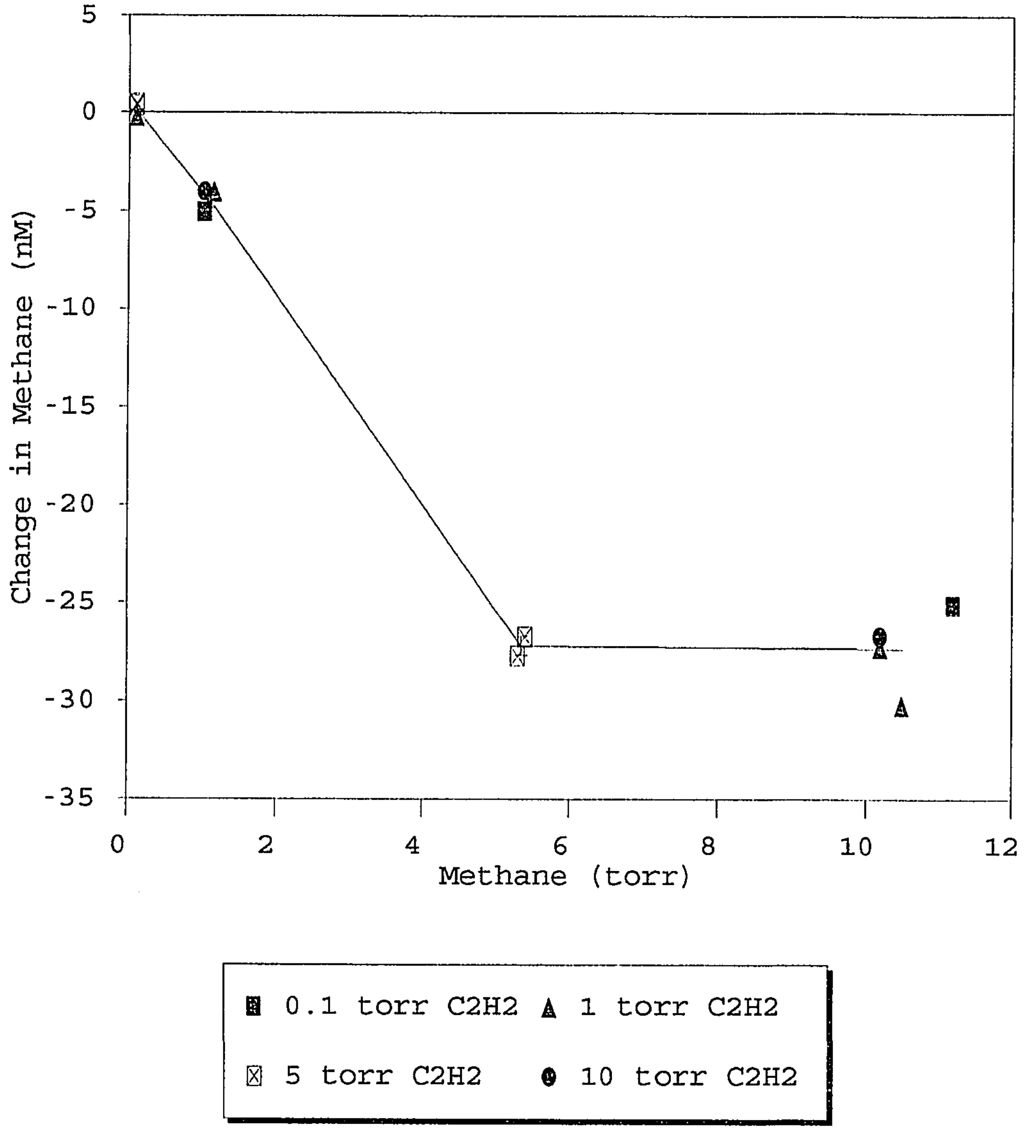

Fig. 3.10: The photosensitized decomposition of methane was observed by the decrease in methane remaining in the samples of acetylene, methane, and nitrogen ($C_2H_2/CH_4/N_2$). The change in methane is dependent on the methane pressure and independent of the acetylene pressure.

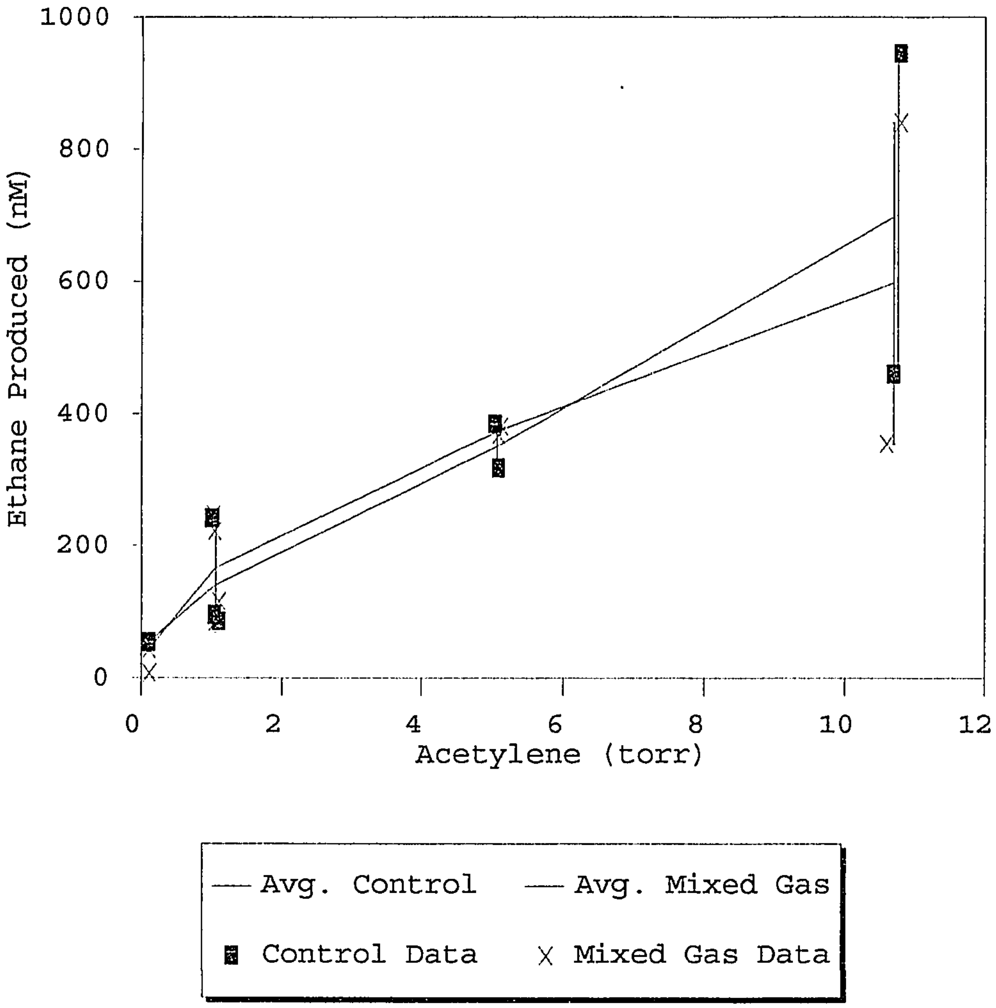

Fig. 3.11: A comparison of the concentration of ethane produced in the $C_2H_2/CH_4/N_2$ and C_2H_2/N_2 samples. There was little or no change in the ethane produced by the photolysis of acetylene with or without the addition of methane.

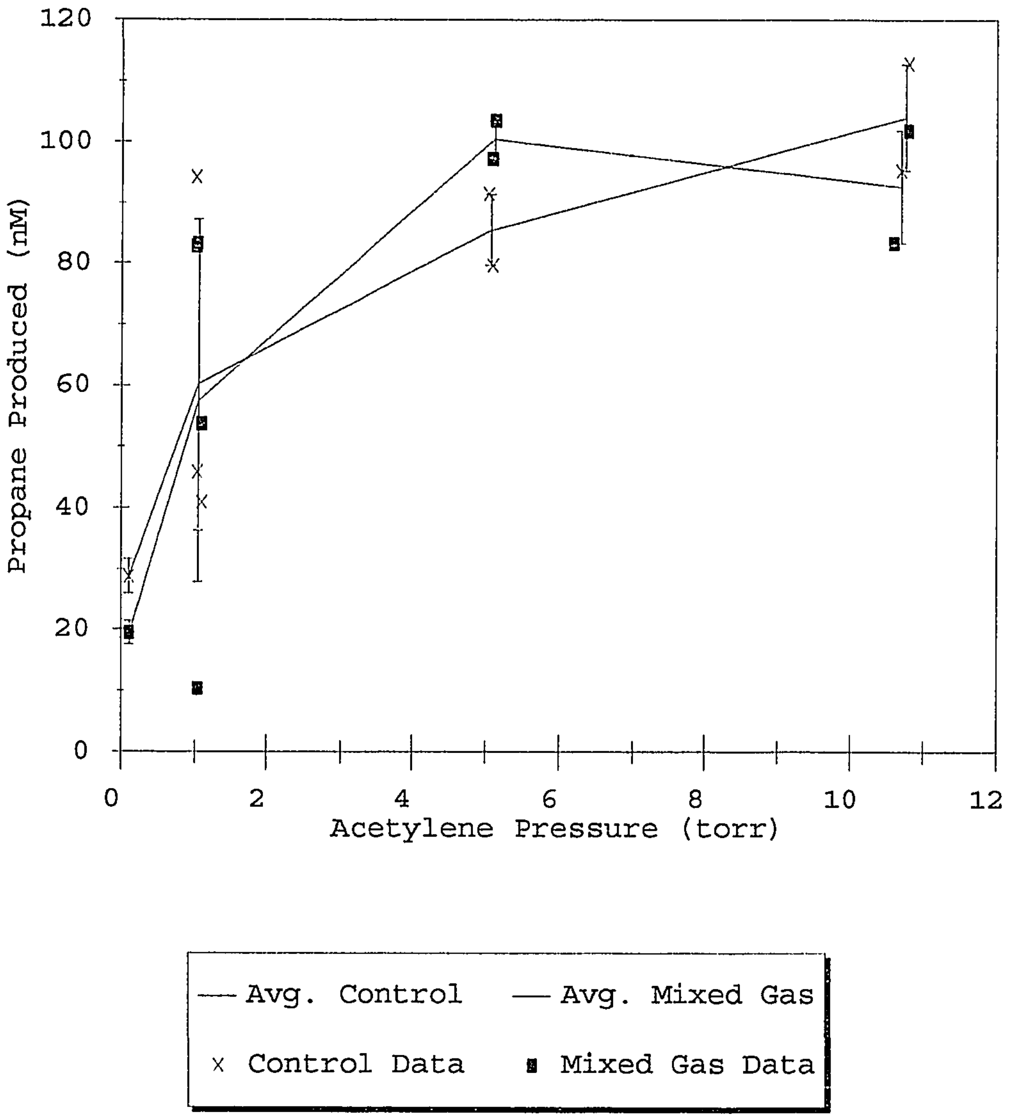

Fig. 3.12: A comparison of the production of propane from the photolysis of acetylene, methane, and nitrogen and the control. There was little or no change in the amount of propane produced, as was observed in the ethane results.

4. Conclusion

The photochemistry in the stratosphere of Titan is dominated by hydrocarbon reactions due to the abundance of methane. Acetylene is the primary product of the photolysis of methane. Several experiments have been performed to simulate and study the subsequent photochemistry of acetylene in Titan's stratosphere. Titan's stratosphere contains three organic haze layers that envelop the satellite. Laboratory simulations were performed to experimentally model the production, size, and aggregate distribution of polyacetylene aerosols that are believed to make up these haze layers. The formation of these aerosols was also studied as a function of background gas pressure. Finally, the formation of the head space gases were studied to better understand the observed mixing ratios of those gases in Titan's stratosphere.

The photolysis of acetylene produces polyacetylene molecules that aggregate and produce aerosol particles. It is believed that these are similar to the particles that make up the 3 stratospheric haze layers observed in the stratosphere of Titan. The size distribution of the aerosol particles was observed to be gaussian. It was shown that the mean particle radius of the aerosol particles produced in the laboratory by the photolysis of acetylene is dependent on the acetylene pressure. As the acetylene pressure increased from 0.2 to 10 torr, the mean particle radius increased from 0.2 to 0.4 um. A study of the frequency of aggregates showed that most of the particles were observed in aggregates. However, the most frequent aggregate category was either single particles or aggregates containing two particles. As the number of the particles per aggregate increased, the total number of aggregates observed decreased.

The overall rate of aerosol appearance was studied as a function of the overall pressure. As the total pressure increased from 0 to approximately 60 torr, the time it took for the particles to scatter the laser beam decreased from 10.5 minutes to about 1 minute. At total pressures greater than 60 torr, there was little or no change in the time it took for the aerosols to scatter the beam. It appears that the overall rate of aerosol appearance is dependent on the total pressure at total pressures less than 60 torr. This rate dependence might be due to the need for a collision partner in the formation of the aerosols. However, it is unknown where in the reaction mechanism this is necessary.

Finally, the photolysis of acetylene also produces other hydrocarbons. In a one hour acetylene photolysis experiment, ethylene was the primary product, followed by equal amounts of ethane and methane, and finally propane. Additional hydrocarbons are also sometimes observed but were not quantified and are not expected to be produced in concentrations greater than that of propane.

The amounts of ethane and propane in the stratosphere are greater than in the tropopause, the region of the atmosphere where the temperature is at a minimum. The increased mixing ratio must be photochemically produced, due to the tropopause temperature restrictions. It has been suggested that the increased mixing ratio of ethane and propane was the result of photosensitized decomposition of other hydrocarbons by acetylene.[1] The production of ethane would be the result of the catalytic decomposition of methane by the photolysis of acetylene.[1] When acetylene was photolyzed in the presence of methane, the decomposition of methane was observed. The decomposition of methane was dependent on the methane pressure and independent of the acetylene pressure. The amount of ethane produced by the photolysis of acetylene with or without methane was compared to determine how much this increased the abundance of ethane. The results showed that there was no change in the amount of ethane produced. Therefore, the catalytic decomposition of methane by the photolysis of acetylene doesn't account for the increased ethane in Titan's stratosphere. The same result was observed for the production of propane. However, production of propane by photosensitized decomposition was not conclusive because the production of propane was also dependent on the increased presence of ethane.

Many new experiments can be developed from this research. It is probable that the photolysis of acetylene produces aerosol particles smaller than 0.1 um in diameter. Experiments with a new High Sensitivity Laser Aerosol Spectrometer recently delivered to our group should help detect particles as small as 0.065 um in diameter. The formation process and composition of the polyacetylene aerosol particles are unknown. It has been suggested that Laser Desorption Mass Spectroscopy could be used to determine the composition of the aerosol particles. Finally, laboratory simulations at room temperature are much different than reality on Titan. More realistic simulations of the formation of Titan aerosols might include low temperature, microgravity experiments. A photolysis cell has been constructed that will control the cell temperature at temperatures as low as 125K, 45K lower than the temperature in Titan's stratosphere. It is hoped that low temperature experiments will eventually be performed on one of the NASA Space Shuttles so that more realistic low gravitational simulations may be completed.

5. Appendices

Appendix A

Ammonia Actinometry

A low pressure mercury lamp was used to photolyze the gas samples used in this study. The irradiation output of the lamp was monitored to make sure that large changes did not occur. The lamp flux is the number of photons emitted by the lamp per unit time. The lamp flux at 185 nm was measured by ammonia actinometry.

Two UV-Vis spectrophotometry cells were filled with 4 torr Matheson brand electronic grade ammonia. The absorption spectrum between 215 and 219 nm was taken 5 times with a Cary 3 spectrophotometer before and after photolysis. The maximum absorption was measured and the average and standard deviation was calculated. The amount of ammonia photolyzed over a fixed amount of time, usually 600 sec., was dependant upon the lamp flux. The percent change in the absorption of ammonia before and after the photolysis equals the percent change in the ammonia pressure in the actinometry cell.

$$\%\Delta A=\frac{A_i-A_f}{A_i}=\%\Delta P \qquad (1)$$

In equation 1, A_i and A_f were the average maximum absorption of the ammonia before and after photolysis, respectively. From the ideal gas law, the change in moles, n, of ammonia were calculated:

$$\Delta n=\frac{\Delta P*V}{RT} \qquad (2)$$

where delta P is the change in ammonia pressure, V is the volume of the actinometry cell, R is the gas constant, and T is the temperature. Using Avogadro's number, the change in molecules could be calculated. The quantum loss (ϕ) of ammonia at 185 nm is 0.26 molecules per photon.[1,2] The flux of the lamp was finally determined by equation 3 in photons per second.

$$Flux=\frac{\Delta molecules}{\phi*t\,(\mathrm{sec})} \qquad (3)$$

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Appendix B

Analysis by Gas Chromatography

Analysis of the head space gases consumed and produced were performed by gas chromatography. In order to determine the contents of the cells, extractions of the samples needed to be injected into the GC resulting in a change the contents of the cell. The loss of the extracted samples needed to be corrected for in the analysis of the contents. The following is a derivation of the correction and analysis calculations.

From the ideal gas law, the initial contents of the cell were:

$$P_i V_{loop} = n^i_{loop} RT \qquad \textbf{(1)}$$

where i represents the initial conditions before expansion and n^i_{loop} and V_{loop} are the moles of sample with the initial pressure and loop volume. After the first expansion:

$$n^1_{loop} = \frac{P_{loop} V_{loop}}{RT} \qquad \textbf{(2)}$$

where loop represents the conditions after expansion into the loop. Given that the pressure will decrease with increasing volume at constant temperature:

$$P_{loop}V_{total}=P_iV_{bulb} \tag{3}$$

where V_{total} is the volume of the bulb plus the loops and V_{bulb} is the volume of just the bulb. Solving equation 3 for P_{loop} and substituting into equation 2:

$$n^1_{loop}=\frac{P_iV_{bulb}V_{loop}}{V_{total}RT} \tag{4}$$

Solving equation 1, for P_i and substituting into equation 4 gives a recursion formula in the form:

$$n^{i-1}_{loop}=n^i_{loop}\frac{V_{total}}{V_{bulb}} \tag{5}$$

The ratio of the total and bulb volumes is defined as the expansion ratio (ER). Rearranging equation 5, the ER for a given bulb and injection port is equal to the ratio of consecutive GC responses:

$$\frac{V_{total}}{V_{bulb}}=\frac{n^{i-1}_{loop}}{n^i_{loop}}=\frac{Response^{i-1}}{Response^{i}}=ER^{i} \tag{6}$$

Therefore, the ER was determined by injecting methane from a specific photolysis cell 11 times and calculating the ratio of the area counts, and the average and the standard deviation. The ER was determined for every cell used because each cell has a different volume.

When making extractions from the photolysis cell, the area counts were corrected using the average ER for that cell:

$$AC=\frac{Response}{ER^{i}} \tag{7}$$

In equation 7, AC is the area corrected counts, i is the expansion number, and ER^i will correct the area counts back to the initial conditions. The average area corrected counts and standard deviation were calculated and used to determine the molar response (MR) of the standard.

The molar response (MR) is defined as the area counts per mole, which is simply the slope of the calibration curve. Calibration curves were done for methane and acetylene to verify that the curves were indeed linear and are shown in Fig. 2.2a and b. However, the MR for a given experiment was determined from the standard samples taken that day. If the initial pressure in the cell was known while the ER was being determined, the MR could also be calculated. The MR for each of the standard gases were calculated by:

$$MR_{avg} = \frac{AC_{avg}}{n^{o}} \qquad \textbf{(8)}$$

where n° are the moles of standard initially in the loop.

When determining the unknown amount of a gas in the sample, the area counts were corrected as in equation 7. The moles of sample expanded into the loop was calculated by dividing the MR from equation 8 into the area corrected counts:

$$n_{1} = \frac{AC_{sample}}{MR_{STD.avg.}} \qquad \textbf{(9)}$$

These calculations became increasingly complicated when multiple extractions were taken before and after photolysis. The amount of gas extracted needs to be accounted for as gas extracted and not as gas that reacted during photolysis. The moles remaining in the sample after extraction were calculated from the chromatograph without correcting for expansion. The moles remaining in the cell before extraction were corrected to account for the extraction of the sample by multiplying it by the ER. Therefore, the change moles of gas in the sample were calculated to be the difference in moles without correcting the area counts of the previous expansion and the corrected counts of the current expansion:

$$\Delta n = n^{i-1}_{uncorr} - n^{i}_{corr} \tag{10}$$

The change in moles was than subtracted from the corrected moles of the previous experiment to give the corrected concentration. This was not a problem with the standards because the expansions were consecutive and no change in composition occurred between expansions.